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PRINCIPLES

OF

QUANTITATIVE ANALYSIS

AN INTRODUCTORY COURSE

BY

WALTER C. BLASDALE, PH. D.
Associate Professor of Chemistry in the University of California

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SECOND EDITION REVISED AND ENLARGED

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70 *ILLUSTRATIONS*

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PREFACE TO THE SECOND EDITION

THE changes which have been made in preparing the second edition of this book, aside from the rectification of the typographical errors which crept into the first edition, are relatively few. Certain sections, which experience in the use of the book had shown to be too condensed, have been expanded and the material in certain other sections has been rearranged or entirely rewritten. Many of the problems have been modified or others believed to be more instructive have been substituted. The suggestions made by a number of instructors who have used the book that answers to the problems be given, has been acted upon and answers to many of the more complex numerical problems are now included.

The results obtained in the use of the book have confirmed the author in his belief that the statements made in the preface to the first edition are correct and that the method of presenting the subject of quantitative analysis which has been adopted is an improvement over that heretofore in general use, at least where students of a sufficient degree of maturity are concerned and where the training which it is desired to give them is not of a specialized character.

W. C. B.

BERKELEY, CALIFORNIA
October, 1916.

PREFACE TO FIRST EDITION

THE introductory course in quantitative analysis is expected to meet a variety of needs. For a limited number of students it represents the beginning of a course of training which ultimately leads to the ability to do effective work as a professional analyst. For others it represents merely one of the necessary features of the training, which every student who aspires to the title of chemist must complete. For still others the object to be gained is a general survey of the methods of quantitative analysis, and the ability to comprehend and make intelligent use of the results obtained by it, especially as applied to the various branches of both pure and applied science.

Some of the other difficulties which arise in presenting the subject are, the limited amount of time which can be devoted to it; the large amount of personal supervision and assistance which should be given each student, if he is to acquire the necessary manipulative skill with the least expenditure of time and effort; and the inability of the instructor to furnish the student with an adequate supply of platinum ware and of many of the conveniences and special forms of apparatus, with which it is desirable the student should become acquainted.

In this book the attempt has been made to meet these difficulties by outlining the entire field covered by the subject; that is, by presenting it from the standpoint of a comprehensive scheme of classification, which is based upon the different types of chemical and physical equilibrium. By adopting this method of presentation it becomes readily possible to discuss the theory of all classes of quantitative processes from the point of view of modern theoretical chemistry, which forms the only logical basis for effective work in analytical chemistry, and incidentally to

add to the student's experience in dealing with the factors which affect equilibrium.

After the general theory underlying each type of process has been presented, a number of examples designed to illustrate it are discussed and described in detail. The number outlined is larger than can be made use of in the introductory course usually given, but can be reduced to a single illustration from each class if necessary. Altho especial emphasis has been placed upon its theoretical features, the fact that the subject is essentially a practical one, and that the student's interest is most easily maintained when he is required to solve practical problems, the results of which cannot be foretold, has not been lost sight of. Hence a large number of the illustrations chosen are practical problems, which have been selected from a variety of fields and which are solved by the use of methods employed in practical work. It is assumed that as far as possible, individual samples, whose composition is known only to the instructor, will be given out for these determinations.

In the development of these illustrations, the attempt is made to make use of as great a variety of principles and methods of procedure as possible, and to develop the student's ability to make use of them by assigning for solution a series of questions and problems; those outlined are offered as suggestions only, and should be modified from year to year.

It is scarcely necessary to add that most of the ideas which have been made use of are not new. Especial acknowledgment should be made to Ostwald, whose "Grundlagen der analytischen Chemie" represents the first attempt to summarize those features of theoretical chemistry which can be most profitably applied to analytical chemistry. Acknowledgment of some of the other sources of information will be found in the text, but the limitation imposed on the size of the book has made it impossible to acknowledge all of them.

W. C. B.

BERKELEY, CAL.
July 1, 1914.

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QUANTITATIVE CHEMICAL ANALYSIS

CHAPTER I

INTRODUCTORY STATEMENTS AND DEFINITIONS

Importance of Quantitative Analysis. Quantitative analysis has for its object the determination of the quantity of some element or compound present in a particular substance. The result of the determination is usually expressed as a percentage, ordinarily by weight, but sometimes by volume, of the substance concerned.

The subject is of importance from a number of standpoints. An accurate evaluation of most of the important objects of commerce, and determination of their fitness for certain purposes, cannot be made until their quantitative composition has been determined. In many manufacturing industries the raw products used are purchased, and the finished products obtained are sold, on the basis of the results shown by their analysis; further, the entire process of manufacture is often controlled by means of analyses of the various products, for such analyses enable the manufacturer to determine whether each of the various stages of the process have been properly carried out, and to reduce wastes and losses to a minimum.

In the study of many branches of natural science the investigator is often obliged to depend upon quantitative analyses for the identification and comparison of the substances with which he is concerned, and is frequently enabled to trace the laws which govern the changes taking place in these substances thru the study of the results of their analysis. The present science of chemistry

is based very largely upon the employment of quantitative methods in the study of chemical changes; the sciences of geology and physiology have been very largely developed by the use of data gathered thru the employment of quantitative methods.

The subject has also a certain educational value, in that it concentrates the attention of the student upon a limited number of chemical transformations; teaches him to observe critically all of the changes which take place in the material with which he is dealing, and to devise methods of avoiding certain undesirable effects and take advantage of others which are desirable.

Range of the Subject. It is evident from the preceding paragraphs that the field of quantitative analysis extends over an extremely wide range of subjects, for the analyst may be called upon to determine the quantitative composition of any material object whatever. The analysis of substances containing a number of constituents often presents a problem of much complexity, and much ingenuity has been used in devising methods, which can be employed to determine those elements and compounds, that are of importance from either a practical or scientific standpoint, with the requisite accuracy and with the minimum expenditure of time and effort. The acquirement of a working knowledge of even the more important of these methods is a task of considerable magnitude, and the subject forms one of the most comprehensive branches of the science of chemistry.

Types of Quantitative Processes. A sufficiently comprehensive and entirely satisfactory classification of all the methods included under the general head of quantitative analysis is not easily formulated. All of the more important methods in general use may be grouped under four classes, which differ so fundamentally in method of procedure that it is desirable to discuss them separately.

Gravimetric methods are those in which the determination is effected by the actual separation of the desired constituent, or some product which bears a definite quantitative relation to it,

and the determination of the weight of the product thus separated. Thus the silver can be determined in an alloy by dissolving a definite weight of the alloy in nitric acid, separating the silver present as insoluble silver chloride, weighing the latter, and calculating the weight of silver present from the factor representing the ratio of the atomic weight of silver to the molecular weight of silver chloride.

The distinguishing feature of all gravimetric processes is the mechanical separation of a product, the weight of which bears a known relation to the weight of the substance which is being determined, from the substance being analyzed. Such separations are possible only when there are definite surfaces, which represent the limits of the spaces occupied by the separated substance on the one hand, and the residual mixture on the other. Expressed in the language of modern theoretical chemistry every gravimetric process involves a series of chemical and physical operations, which bring about such changes in the original substance that a new "phase" separates, the term phase being used to designate a mass of matter which is physically and chemically homogeneous. In the illustration cited the separated phase took the form of a solid; it might have taken the form of a gas, or of a second liquid, which does not mix with the first, and a logical and convenient basis for the classification of gravimetric processes is found in the type of "phase-transformation" which they represent. Such a scheme has been adopted in this book, and separate sections are devoted to "gas evolution processes," in which a new gas phase is made to separate from a solid or liquid; "precipitation processes," in which a new solid phase is made to separate from a liquid; "solution and extraction processes," in which a new liquid phase is made to separate from a solid; and "partition processes," in which a new liquid phase is made to separate from a liquid phase.

Volumetric methods are those in which the amount of substance to be determined is estimated by measuring the volume of some reagent of known concentration, which must be used to completely

transform the constituent being determined into some other form. The actual separation of a particular product is thereby avoided. Thus the silver can also be determined in the alloy by measuring the amount of sodium chloride solution of known strength which must be added to a solution containing a known weight of the alloy to precipitate all of the silver as chloride. Volumetric processes are conveniently classified with respect to the type of reaction upon which they are based; the three important classes are made the subject of separate sections of this book.

Physico-chemical methods are those in which the unknown substance is determined by measuring some one of the various physical properties of a solution containing a known concentration of the sample under investigation, and comparing with the corresponding properties of solutions containing known concentrations of the substance to be determined. They are of rather restricted application, and are not strictly speaking chemical processes, but they are so frequently used by the analytical chemist that it is customary to group them with these.

Gas-analysis methods which are based upon the direct measurement of gas volumes form still a fourth group. They are used not only for the analysis of gaseous mixtures but also for the determination of a large number of substances which yield gaseous products when submitted to the action of certain reagents. The successful use of these methods demands the employment of a large amount of specialized forms of apparatus; it has not been thought desirable to consider them in this book.

The Training and Skill Required. Success in quantitative work demands first of all a certain amount of dexterity in performing the mechanical operations involved. Training of the hand and eye, which results in the formation of habits of deftness and precision in manipulation is an essential prerequisite to work in this field. Certain individuals are able to acquire this skill with comparative ease, but, unfortunately, by far the great majority of persons can acquire it only thru patient and persistent appli-

cation. The beginner cannot be expected to do as rapid or as accurate work as the trained analyst, and only actual experience with a great variety of quantitative processes will teach the most effective methods of dealing with the problems which constantly arise in the execution of quantitative work and enable him to reduce to a minimum those errors of the process which depend upon manipulative skill.

Absolute Honesty Demanded. Of the many qualifications which the successful analyst must possess none equals in importance that of unimpeachable honesty. It is unnecessary to condemn or to point out the ultimate effect of the intentional falsification of the results obtained in any line of scientific work to any intelligent student; but even when there is no desire to misrepresent, care must be taken to overcome any temptation which may arise to pick and choose results on the basis of some preconceived notion of their comparative accuracy. If, for example, a number of results have been obtained with the same process, the fact that some one of these agrees most nearly with what is supposed to be the correct result does not justify suppressing the others, unless there is positive evidence of the fact that they involve errors which do not appear in the one which it is proposed to accept. If the student finds himself unable to do as good work as a more experienced or more fortunately endowed neighbor he should not hesitate to frankly acknowledge the fact, and should devote his efforts to increasing his proficiency rather than to concealing his lack of it. Deficiencies of this kind can be overcome thru intelligent and well-directed effort, and the satisfaction which results from overcoming them is well worth the effort which it may cost. The ability to do good analytical work represents a non-transferable asset of no small commercial value.

Theoretical Knowledge Necessary. Altho any person who has acquired the necessary manipulative skill may be able to execute the details of a carefully described quantitative process, his ability to make effective use of the process will be decidedly

limited, owing to the fact that unforeseen contingencies, which his carefully worded description did not allow for, constantly arise. It is only thru a definite knowledge of the theory of each step of the process that the analyst can work intelligently and effectively; the mechanical performance of such operations without understanding the reason for each step is not worthy of being dignified by the term "quantitative analysis."

It should also be noted that the method employed must be adapted to the purpose for which the desired result is to be used. Frequently the rapidity with which a result can be obtained is of greater importance than extreme accuracy, and in such cases time and labor can be saved by neglecting certain of the details commonly used or by employing certain "short-cut" methods. Every quantitative determination is, therefore, a specific problem in itself, and an analysis of the various factors concerned in every detail of the proposed method may render it possible to increase either the accuracy of the work, or the productive capacity of the analyst. An accurate sense of proportion and judgment, as to the importance and necessity of the details of quantitative work must be developed if the greatest efficiency is to be attained.

The Literature of the Subject. A vast amount of experimental work having for its object the development of new, or perfection of old, methods of analysis is being carried out continually. The results are published either in certain special journals devoted to this branch of chemistry, such as the Zeitschrift für analytische Chemie (Wiesbaden) and the Analyst (London) or in the more numerous chemical periodicals of a more general character. Especial importance should be attached to the reports of Committees and Associations, who coöperate in making tests of analytical methods under as nearly identical conditions as possible. Such, for instance, is the work of the Official Association of Agricultural Chemists or of the various Committees of the American Chemical Society. The progressive analyst will find it necessary to keep in touch with the newer

developments of the subject, and even the beginner will derive much profit and inspiration from consulting the original sources of information upon which the methods he uses are based; hence, references to a limited number of important articles are added to some of the processes described in this book. Altho a number of works which attempt to summarize all of the more important quantitative methods are available, more comprehensive and usually more up-to-date information can be found in the numerous manuals devoted to the elaboration of the methods which are especially adapted to the analysis of particular classes of materials, such as ores and metallurgical products, alloys, rocks, soils and fertilizers, foods, etc.

Proposed Plan of Work. The object of this book is to present the fundamental principles used in the general subject of quantitative analysis, and outline a method by which a working knowledge of the subject can be attained. In the plan of work here adopted the theory of each of the larger groups of quantitative processes is first discussed, then a limited number of typical illustrations are described in detail and the various sources of error and further applications of the method suggested. A series of questions and problems designed to point out the reasons for certain features of the methods and emphasize the general principles used are appended to most of these descriptions. In the elaboration of each of the different classes of processes much matter of a more general character finds constant use; this has been presented in brief form in the series of chapters forming the first section of the book. Familiarity with all of the facts there presented is not an essential prerequisite to actual work with the methods described in the subsequent sections; all of it is necessary to a comprehensive knowledge of the principles of quantitative analysis, and these chapters should be carefully read and digested as progress is made in the practical part of the work.

Strength of Reagents Used. A large number of the reagents used in quantitative analysis are prepared for one specific purpose

only; the method of preparing such reagents will be given in the descriptions of the processes in which they are used. The strength of certain reagents which are used in a great variety of processes are given below.

Dilute ammonium hydroxide, made by adding one and one-half volumes of water to one of concentrated ammonium hydroxide (sp. gr. 0.9). One cc. of the diluted reagent contains 0.102 gm. NH_3. It is 6-normal.

Dilute acetic acid, made by adding one and four-tenths volumes of water to one of 80 per cent acid. One cc. contains 0.36 gm. $C_2H_4O_2$. It is 6-normal.

Concentrated hydrochloric acid. One cc. contains 0.44 gm. HCl. Its specific gravity is 1.19. It is 12-normal.

Dilute hydrochloric acid, made by adding one volume of water to one of the concentrated acid. One cc. contains 0.22 gm. HCl. Its specific gravity is 1.10. It is 6-normal.

Concentrated nitric acid. One cc. contains 0.99 gm. HNO_3. Its specific gravity is 1.42. It is 15-normal.

Dilute nitric acid, made by adding one and six-tenths volumes of water to one of concentrated acid. One cc. contains 0.38 gm. HNO_3. Its specific gravity is 1.2. It is 6-normal.

Concentrated sulfuric acid. One cc. contains 1.77 gm. Its specific gravity is 1.84. It is 36-normal.

Dilute sulfuric acid. Made by adding one volume of the concentrated acid to five of water. One cc. = 0.30 gm. H_2SO_4. Its specific gravity is 1.19. It is 6-normal.

SECTION I

GENERAL FEATURES OF GRAVIMETRIC PROCESSES

CHAPTER II

THE METHOD OF WEIGHING

I. Theory of the Use of the Balance

Construction. Quantitative processes involve determinations of the relations existing between two masses of matter, but since both masses are determined by means of a beam balance under identical conditions the distinction between mass and weight can be disregarded. The accuracy of such processes must depend in part upon the accuracy with which the two weighings are made, and instrument makers have developed certain forms of balances known as "analytical balances" the use of which makes it possible to reduce the errors from this source to insignificant proportions. The details of the mechanism used by different makers for the adjustment and protection of such balances vary, but since all are based upon the use of essentially the same principles, only one type will be described here.

The beam of such a balance is represented in Fig. 1. It is constructed of such material, and in such a form, as to combine the maximum degree of rigidity and strength, with the minimum weight. It is suspended at its center on a horizontal axis, which is made of agate and accurately ground to a knife-blade edge, as shown at *A* of the figure. This axis rests upon a strip of polished agate supported upon the top of a pillar, and the beam is free to turn in a vertical plane about this axis. Two other knife-blade

ges B and B', which are of a similar construction, but with edges
rned upwards instead of downwards, are fixed at the two ends
d equidistant from the center. These edges sustain specially
nstructed stirrups, which are also provided with strips of agate,

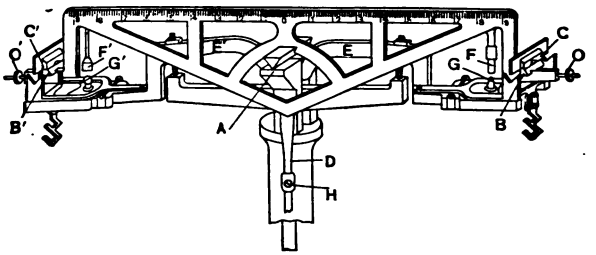

Fig. 1. — Beam of an Analytical Balance

C and C' of the figure, at the points of contact; from them are suspended two pans, one of which supports the substance being weighed, and the other the weights used. The beam may be regarded as a compound lever in which the fulcrum is at the axis of suspension. If the two arms are of equal length, and if the pans and the loads which they contain are of equal weight, the effect of the force of gravity upon the two ends of the beam is identical, and a depression of one end of the beam will produce a series of vibrations similar to those of a pendulum.

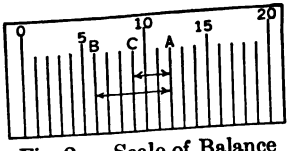

Fig. 2. — Scale of Balance

The process of weighing consists in placing the substance whose weight is to be determined in one pan, and adding weights to the other until the two counterbalance each other. This point can be recognized by observing the movements of the beam, and a pointer, the upper part of which is shown at D, is attached to it for the purpose of magnifying these movements; a small ivory scale, represented by Fig. 2, is placed just back of the end of the pointer, in order to make it possible to measure and record the magnitude of these movements with respect to the central axis.

The center of this scale, which is directly below the axis of suspension, should be marked 10, the tenth division to the left zero, and the tenth to the right twenty; this method of marking the scale at once indicates whether the numbers recorded are to the left or the right of the center.

As the movement of the beam is greatly retarded by friction, and as the friction losses increase very rapidly as the knife-blade edges lose their sharpness, it is necessary to protect these bearings against needless wear; hence, analytical balances are often provided with two sets of rests, known as "beam-rests" and "pan-rests" respectively. The beam-rests are controlled by a milled button, placed at the center and on a level with the floor of the balance case. When rotated it turns an eccentric, which raises a rod passing thru the center of the pillar of the balance, and this in turn raises two hinged arms E and E', which lift the knife-blade edge A from the agate plate, and also the stirrups sustaining the pans from the knife-blade edges B and B' on which they rest. The hinged arms are also provided with two studs F and F', which fit into a cup and a trough terminating the two studs G and G', fastened to the beam. The effect of raising and lowering the beam-rests is to bring the beam into exactly the same position with respect to the agate plate upon which it rests.

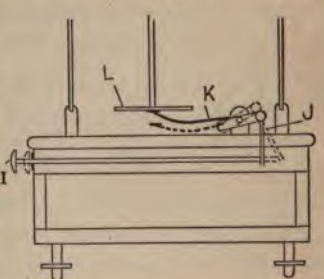

Fig. 3. — Base of Balance Case

The pan-rests are controlled by a small knob placed at the left of the center, as shown at I of Fig. 3. When a slight pressure is applied to this button, the rod to which it is attached moves the lever J which carries two arms K and K' and cause these to drop. Ordinarily these arms impinge upon the bottom of the pans L and L' and prevent needless vibration and wear of the bearings B and B', but when they drop the beam is free to vibrate. As a protection

against dust, moisture and air currents, the entire apparatus is enclosed in a glass case, one side of which consists of a movable slide of the same material.

Conditions which Determine Accuracy. An accurate comparison of the relative magnitudes of two masses cannot be made with such a balance unless certain essential conditions are complied with.

First, the point of suspension of the beam should be equidistant from the points of suspension of the two pans, for if these distances differ the loads sustained by the two arms act with unequal leverages. If the total length of the beam is known the difference in the lengths of the two arms can be calculated from the weights found to be necessary to counterbalance the same object, when placed first on one pan and then on the other. If we represent the length of the right arm by r, that of the left arm by l, the true weight of the object by W, the apparent weight when placed in the left pan by A, and when placed in the right pan by $A + a$, we have,

$$Ar = Wl, \quad \text{also} \quad Wr = (A + a)\, l.$$

If we multiply these two equations together and simplify the resulting expression we can obtain the relation

$$(r)^2 : (l)^2 :: A + a : A.$$

It is also easy to show that the true weight of the object corresponds to the square root of the product of the two apparent weights, or since the two differ but slightly, it is represented with sufficient accuracy by the average of the apparent weights. Since it is not possible to make a balance whose two arms are absolutely equal, this method of "double weighing" is always used where extreme accuracy is demanded. The error which might result from this defect in the construction of the balance can usually be neglected if the same pan, usually the left-hand one, is used for all weighings concerned in the analyses.

d, the center of gravity of the entire system, that is, of the the two loads which it sustains, must be slightly below

the point of suspension of the beam. If the reverse relation holds, the system is in unstable equilibrium; if the two points fall together, the system is in neutral equilibrium, and vibration of the beam even with equal weights is impossible. If the center of gravity of the system is too far below the point of suspension, the deflection produced by a slight excess of weight in either pan is but slight, and the balance is not sufficiently sensitive. By means of a small weight, which slides up and down the pointer, but which can be fixed by means of a set screw, see *H* of Fig. 1, the center of gravity can be lowered or raised. If, however, this distance is made too small the retarding effect of friction is relatively greater, and the movements of the beam are slow and uncertain.

Third, the point of suspension of the beam and of the two pans must be very nearly on the same horizontal line; otherwise, changes in the loads carried by the pans change the position of the center of gravity, and hence the sensitiveness. Since all balance beams yield slightly to heavy loads it is impossible to comply with this condition in all cases. Manufacturers usually endeavor to make *A* stand as much below the line joining *B* and *B'*, when the balance is empty as it stands above this line when the pans sustain the maximum permissible load; the balance should then show the minimum change in sensitiveness with an average load.

Sensitiveness. The sensitiveness of a balance is measured by the magnitude of the angle, corresponding to the change in the position of the pointer, produced by a slight excess of weight in either pan. Evidently this angle must increase as the length of the beam is increased, but it is undesirable to increase the length of the beam beyond a certain maximum, as the movements of the pointer then become correspondingly slow (and in this respect the behavior of the beam differs from that of a pendulum), and the time occupied in making a weighing is materially increased. The sensitiveness decreases as the weight of the beam and the other factors which produce friction increase. The third, and perhaps most important, factor is the adjustment of the center of gravity

with respect to the point of suspension. The quantitative expression which represents the relation between these factors is given by the equation:

$$\text{Tan } \alpha = \frac{L \times W}{D \times Q},$$

in which L is the length of the arm, W the excess of weight in the pan, D the distance referred to above, and Q the weight of the beam.

As ordinarily used the term sensitiveness represents the number of scale divisions thru which the pointer is deflected by one milligram. Altho it is desirable to make the sensitiveness large by reducing the value of D, it cannot be reduced below a certain limit, which depends largely upon the skill used in the construction of the balance and the weight of the beam, or the movements of the pointer become so variable and uncertain that the point of rest cannot be determined with certainty. It should be possible to so adjust the balance that it has a sensitiveness of from 1.5 to 2 divisions.

The Point of Rest. If we have an ideal balance, that is, one which has been perfectly constructed, which moves without friction, and which is loaded with equivalent weights, a slight depression of one end of the beam will cause the beam to vibrate back and forth and the pointer to move an equal number of divisions to the right and to the left of the central point of the ivory scale for an indefinite length of time. Owing to friction, and various faults of construction, there is a constant decrease in the amplitude of these vibrations, and the beam finally comes to rest. This position, as indicated by the position of the pointer with reference to the divisions of the ivory scale, is called the "point of rest" of the balance, and is constant for any given set of conditions. Owing to slight variations in these conditions, accumulation of dust on the pans, temperature changes, etc., this point may vary slightly from day to day, and rarely corresponds exactly with the center of the ivory scale. If it differs from it greatly the balance should

be readjusted by movement of one of the two buttons, O and O' of Fig. 1, at the end of the beam, toward or away from the point of suspension as the case may require.

The exact position of the point of rest C is most rapidly and accurately determined by noting the limits of a series of vibrations, and averaging the results. If there were no decrease in the amplitude of these vibrations, one-half the sum of the averages of the positions reached by the pointer on the right and left respectively would give the correct position of the point. Owing to this decrement, however, this is strictly true only when an even number of readings is made on one side and an odd number on the other, as consideration of the accompanying diagram, Fig. 4, will show. In this diagram the successive positions reached are designated by the letters of the alphabet. If there were no decrement due to friction the expression

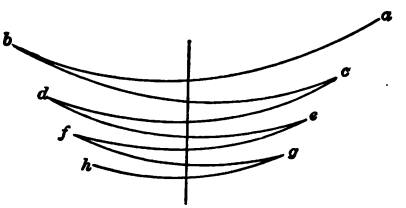

Fig. 4.—Diagram Representing Movement of Pointer

$$C = \left[\frac{(a+c+e)}{3} + \frac{(b+d+f)}{3}\right] \div 2$$

would give the correct position of the point of rest. The positions actually reached differ from those to which the above formula would apply by multiples of the decrement k which is approximately constant. If a be taken as the starting point the position b differs from that which would be attained if there were no friction by the constant k, the position c by twice that constant, the position d by three times the constant, etc. If now we average the two series, the one to the right, the other to the left, for five vibrations, we obtain as the expression for the point of rest, using the corrected values:

$$C = \left[\frac{(a+c+e-6k)}{3} + \frac{(b+d+4k)}{2}\right] \div 2.$$

In solving this expression the value of the constant k is eliminated while if an equal number of readings be taken for the two series this is no longer true.

The Accurate Method of Weighing. Having determined in the manner described the point of rest of the empty balance, the weight of any substance can be determined by placing it on one pan of the balance, and adding weights to the other until the point of rest corresponds to that originally found. If accurately carried out the process is a slow one, and may be abbreviated by an equally exact interpolation process, which depends upon the fact that the change in the point of rest is directly proportional to the weight by which it is produced. In using this method the unknown substance is placed on the left pan and weights added, using milligrams only, until the point of rest is not far from that of the empty balance. If this point of rest is to the right of C another milligram is added to the weights in the pan, and the point of rest again determined, or if it is to the left, one milligram is removed and the point of rest determined. The difference $A - B$, in which A and B represent the points of rest corresponding to the lesser and the greater weights respectively, gives the deflection produced by one milligram. In order to change the point of rest to that of the empty balance $(A-C) \div (A-B)$ mg. must be added to the lesser weight. The interpolation method is represented graphically on Fig. 2, which shows the actual positions of A, B and C, on the ivory scale in a specific case. It is obvious that $(12 - 9) \div (12 - 6)$ or 0.5 mg. must be added to the weight which gave the point of rest A in order to counterbalance the unknown substance in the left pan. The value of $(A - B)$ is not constant unless the load sustained is constant but where these differences are small the changes in this value can be neglected, hence, it is often possible to omit the determination of either A or B if the proper constant has been previously determined. The value of C does not usually differ greatly during the course of a laboratory period, and need only be determined once. This method of weighing is the most

accurate in use and with experience is rapidly executed. Under favorable conditions it should be possible to reduce the error involved in weighing by this process to one-tenth of a milligram, but this represents the extreme limit of accuracy which can be attained with the ordinary analytical balance. If a greater degree of accuracy is demanded a more carefully constructed "assay balance" must be used, but this cannot be employed for weights which exceed 5 grams.

Abbreviations of Accurate Method. In all kinds of quantitative work it is the percentage rather than the absolute error which has to be considered, and where large amounts of material are to be weighed the above method may be shortened. If we are to weigh a precipitate of about the magnitude of one gram, and weigh to within one-tenth of a milligram, the percentage error involved will be one-hundredth, which is insignificant, as compared with the other unavoidable errors of most quantitative processes, and even if the error involved is a half milligram the percentage error is not excessive. If, however, our precipitate weighs two-tenths of a gram an absolute error of a half milligram cannot be safely disregarded. The abbreviation referred to above consists in making a rough mental calculation of the point of rest from a mere inspection of the movement of the pointer. It may be further noted that most of the weighings made actually involve the difference between two weights, namely, the weight of the empty vessel and that of the vessel and substance. If the same point of rest is assumed for both weighings, the same error will appear in both and the difference will give the correct value of the magnitude desired. The point usually assumed is the center of the scale. Hence the process of weighing which may be used in such cases consists in manipulating the weights till the pointer swings to approximately an equal number of divisions on both sides of the center of the scale, making the proper allowance for the decrement in the amplitude of each vibration. The error involved in this method should not exceed three-tenths of a milligram.

Some judgment must be used as to which of these methods of weighing should be employed, but a fairly satisfactory general rule is to use the more accurate method when the quantity weighed is less than three-tenths of a gram.

The Weights Used. Since the results of quantitative processes are usually expressed in terms of the ratio of the substance found to the substance used, and since the same set of weights is used to determine the value of both of these magnitudes, the absolute value of the standard or unit mass employed is of no significance. If the weights used are consistent between themselves, that is, if the different pieces bear to each other the exact relation for which they are used, no error will appear in the final result. If, however, as in the assay of gold and silver ores, the result is to be reported in terms of the money value per ton, the absolute value of the unit of weight employed is of the greatest importance. The sets of weights sold by firms of established reputation are frequently sufficiently accurate for most kinds of work, but the results obtained with them will always be subject to some uncertainty until they have been accurately tested. Such weights should be handled with ivory-tipped pincers and kept in a closed box when not in use. Platinum weights should not change in value even after years of constant use, but aluminum weights are subject to slight corrosion and must be more carefully protected.

The manipulation of very small weights, especially those below 5 mg. in value, is troublesome and is usually avoided by the use of a "rider." This is a piece of platinum or aluminum wire bent in such form as to hang on the beam of the balance, and easily movable from place to place on the beam by means of a rod. If such a rider, whose weight is exactly 5 mg., is placed on the beam of the balance exactly above the point of suspension of the pan containing the weights it would have the same effect as the addition of 5 mg. to that pan, or if placed in any position between this point and the point of suspension of the beam it would

have an effect proportional to its distance from the point of suspension of the beam. If the beam is divided into five equal parts each division would be equivalent to 1 mg. Further subdivision of these large divisions enables one to add tenths of a milligram as desired.

The Calibration of Weights. It is often necessary to accurately calibrate a set of weights. This involves first a determination of the exact relations between the different pieces composing the set, and second a reduction of the values thus obtained to the absolute metric unit or some other convenient standard. The method can be readily illustrated by a concrete example. In this work the 5 mg. weight was temporarily adopted as a standard of reference and was found to agree absolutely with the rider of the balance. By comparing systematically the different pieces of the set on an assay balance the results recorded in the accompanying table were obtained. In this table the first column represents the marks on the weight placed in the left pan of the balance, the second column the weights added to the right pan, and the third the position of the rider on the beam of the balance. The figures

5	0	5	5	5
10	5	5	10	10
10'	10	0	10	10
20	10+10'	0	20	20
50	20+10+10'+5	5.08	50.08	50
100	50+20+10+10'+5	5.08	100.16	100
100'	100	0.05	100.21	100.1
200	100+100'	0.05	200.42	200.2
500	200+100+100'+50+20+10+10'+5	5.08	500.95	500.3
1000	500+200+100+100'+50+20+10+10'+5	5.12	1001.94	1000.7

in the fourth column represent a summation of those in the second and third plus the corrections previously found, and hence the values of the different weights in terms of the 5 mg. weight.

The 1 gm. weight was next compared with a standard metric gram on an assay balance and found to have the value 1.00075.

Multiplying the series of figures in the fourth column by the factor (1.00075 ÷ 1.0019), that is, 0.9988, they were reduced to the corresponding values in terms of the absolute metric units and the results which appear in the last column of the table obtained. The figures which appear in the second decimal place have no significance in analytical work and are therefore neglected.

Correction for Buoyancy. The apparent effect of gravity upon any object which is surrounded by the atmosphere is less than the true effect by an amount corresponding to the weight of the volume of air which it displaces. If the loads sustained by the two pans of the balance displace the same volume of air, buoyancy affects both equally, but where the object being weighed, and the weights used to counterbalance it differ in volume, buoyancy affects the load displacing the greater volume of air to a greater extent than the other, and causes a corresponding error. The magnitude of this error can be calculated from the weight of a unit volume of air, and the difference between the specific gravities of the weights and object weighed. If the specific gravity of the sample weighed out for an analysis equals that of the substance separated, buoyancy causes the same proportionate error in the two weighings upon which the final result depends.

The Error Resulting from Hygroscopic Water. Any solid object, which has not been especially dried and maintained in an atmosphere which is free from water vapor, retains a film of hygroscopic water upon its surface. If the surface presented is large the true weight of such an object may differ from the apparent weight, that is, the weight determined under ordinary atmospheric conditions, by several milligrams; and further, the difference varies with the amount of water in the atmosphere. Altho this film of water can be expelled by heating the object to 100° for a few minutes, it is not readily possible to entirely prevent the reabsorption of hygroscopic water while it is being cooled and weighed. A 15-gm. crucible, for example, which has been allowed to cool in a desiccator, and which is weighed in a balance, the case

of which contains a jar of calcium chloride, will frequently show a gain of from one to three-tenths of a milligram on long standing on the balance pan. When it is necessary to weigh accurately to one-tenth of a milligram this becomes one of the most troublesome difficulties to avoid.

Since most weighings are made in some form of a container, such as a crucible or bottle, the weight actually used in the final calculation represents the difference between the weight of the container plus substance and the container, and the error resulting from the absorption of hygroscopic water can often be reduced to negligible proportions by submitting both to exactly the same conditions before weighing. If, for example, the empty crucible and the crucible plus the substance to be weighed are ignited, placed in a desiccator while still warm, allowed to stand for an hour and then weighed at once, the amount of hygroscopic water absorbed by the crucible in the two cases is practically the same, but not exactly so unless the percentage of water vapor in the atmosphere has remained constant. The only error to be considered in such a case is that due to the absorption of water by the substance itself, which can usually be neglected unless it is decidedly hygroscopic. If it is decidedly hygroscopic it becomes necessary to use a closed container. When the container cannot be heated to a temperature necessary to drive off all hygroscopic water, wiping with a dry cloth has to be substituted. When the surface presented by the container is very large, variations in the moisture content of the air may lead to errors which cannot be neglected. In such cases it is desirable to prepare a counterpoise of about the same surface area as the vessel to be weighed, to submit both vessels to the same treatment before both weighings and to substitute the counterpoise for some of the weights employed in both cases. It may be assumed that variations in the atmospheric conditions will affect the amount of water retained by the two vessels to the same extent, and that no error from this source will appear in the difference finally found.

II. Rules for the Use of the Balance

Altho the general facts and principles upon which the use of the balance is based have been presented in the preceding section, there are a number of details of a purely practical nature which must be observed if the balance is to be maintained in good working order. These are elaborated in the form of the series of rules given below.

First, in order to prevent wear of the bearings, and consequent rapid decrease in the sensitiveness of the balance, large weights should never be placed on or removed from the balance pans, unless the beam- and pan-rests are in position; if the weight being added or removed does not exceed 100 mg. the pan-rests alone will suffice. Both rests should always be left in position before leaving the balance.

Second, the floor of the balance case and the pans should be kept perfectly clean. If substances are spilled within the case they should be brushed up at once with a fine brush or cloth.

Third, no solid substances except certain metals and alloys should be placed in contact with the balance pans. No liquids of any description should be brought into the balance case unless retained in tightly stoppered bottles.

Fourth, hot objects should be allowed to cool to a temperature not greatly in excess of the normal temperature of the balance room before being weighed. If this precaution is not taken disturbing air currents are set up within the balance case. For a like reason the slide of the balance case should be kept closed while the movements of the beam are being observed.

Fifth, the weights should always be handled with bone-tipped forceps and should be carefully protected from dust and fumes.

Sixth, if the point of rest of the empty balance differs from ten by more than one unit, or if the balance fails to behave properly, ask the instructor in charge to make whatever adjustments may be necessary.

III. Details of Procedure for Determination of Point of Rest

Seat yourself squarely in front of the balance case so that your line of vision is directly opposite the center of the balance. Release the beam-rests by turning the button at the center of the case, then the pan-rests by pressing the small knob to the left, next gently lower the rider till it rests on the end of the beam and allow it to remain just long enough to displace the pointer about ten divisions on the ivory scale, and finally remove the rider and permit the beam to swing freely. Take an odd number of consecutive readings (five are sufficient) corresponding to the extreme positions reached by the pointer. Add together the averages of the two sets of readings, one set representing all the readings taken on the right of the center, the other all the readings taken on the left of the center, and divide the sum by two. This gives the point of rest of the empty balance. Repeat the determinations till results are obtained whose extreme differences do not exceed two-tenths of a division.

IV. Details of Procedure for the Determination of the Weight of a Watch Glass

Elaborate Method. Hold a clean watch glass over a gauze heated by the flame of a burner until it is decidedly hot to the touch, then place on a clean support inside a desiccator and allow to cool for twenty minutes. Transfer the glass by means of clean dry pincers to the left pan of the balance and add in regular succession weights of decreasing value to the right pan until the correct weight is determined to within 10 mg. if the balance is provided with a 10-mg. rider, and to within 5 mg. if it is provided with a 5-mg. rider. Next vary the position of the rider on the right arm, placing it at points corresponding to entire milligrams, until the weight is found to within 1 mg. Finally determine accurately the point of rest, first, with the rider in the position

which makes the total weights used slightly less, and second that which makes the total weights used slightly greater than that of the watch glass. These relations can be determined by noting whether the pointer swings decidedly to the right or the left as the changes are made.

Let A represent the point of rest found with the lesser weight, B that found with the greater weight, and C the point of rest of the empty balance. Calculate the correction, expressed in milligrams, to be added to the lesser weight necessary to shift the point of rest from A to C by dividing $(A - C)$ by $(A - B)$, and add this correction to the lesser weight.

Verify the accuracy of the result by adding, by means of the rider, the fraction of a milligram calculated to be necessary and again determine the point of rest. If the work has been accurately carried out, and if the balance is properly constructed and adjusted, the points of rest obtained should not differ from that of the empty balance by more than two-tenths of a division of the ivory scale.

Make a permanent record of the weight thus obtained in the laboratory notebook, in which all weighings and the data upon which they are based should be recorded when obtained. Disregard all figures beyond the fourth decimal place.

Abbreviation of the Method Outlined. In subsequent work this method of weighing may often be abbreviated. Where the weight actually determined is the difference between the weight of the containing vessel and the weight of that vessel plus another substance, the point of rest of the empty balance may be assumed to be ten. Where the magnitude of the mass weighed is not less than 0.3 gm. the accurate determination of the points of rest may be omitted and the weight determined with sufficient accuracy by changing the position of the rider on the beam until the pointer swings to approximately the same distance on either side of the point of rest of the empty balance, making a slight allowance for the decrease in the value of each successive vibration.

V. Details of Procedure for Calibration of a Set of Weights

Determine the relations between the different pieces composing the set, using the procedure outlined on page 19. It is not necessary to reduce the results to the absolute metric standard.

VI. Questions and Problems. Series 1

1. The right arm of a balance has a length of 150.1 mm., the left arm 150 mm.; the apparent weight of a crucible placed in the left pan is 10.032 gm., what is its true weight?

2. What error would result in weighing a 0.3 gm. precipitate in the crucible referred to above if, first, both empty crucible and crucible plus precipitate are weighed on the left pan, and second, if the crucible is weighed on the right pan and the crucible plus precipitate on the left pan?

3. Show that no error is involved in weighing a precipitate if the point of rest of the empty balance is not actually determined, provided the same value is assumed in weighing both empty crucible and the crucible plus precipitate.

4. A crucible placed on the left pan of a balance is exactly counterbalanced when a weight of 10.05 gm. is placed on the right pan and the rider is at the point marked 8.2 on the right arm; if the right arm is divided into 12 equal divisions and the rider weighs 10 mg., what is the weight of the crucible?

5. The weight of a balance beam is 350 gm., its total length 200 mm., and the pointer attached to it has a length of 180 mm.; if one milligram causes a deflection of 2 mm. at the end of this pointer, what is the position of the center of gravity with respect to the point of suspension? *Ans.* 0.026 mm.

6. What error results from failure to correct for buoyancy in weighing a 10-gm. porcelain crucible, assuming that brass weights with a specific gravity of 8.33 are used, that the specific gravity of porcelain is 2.14 and that one liter of air weighs 1.2 gm.?

7. A crucible is found to weigh 10.0542 gm. when placed on the right-hand pan of a balance and 10.058 gm. when placed on the left-hand pan; what is the true weight of the crucible? If the total length of the beam is 180 mm., what is the difference in the lengths of the two arms? *Ans.* 0.02 mm.

CHAPTER III

PREPARATION OF THE SUBSTANCE FOR ANALYSIS

Theory of Sampling. The amount of substance actually employed in making a quantitative analysis is comparatively small, and the result obtained is of but little value unless the portion actually used accurately represents the average composition of the entire mixture. In the analysis of gases and liquids homogeneous mixtures are very easily obtained by a slight amount of stirring, but in the analysis of solid mixtures it is usually necessary to prepare a "sample." The difficulties which arise in preparing a representative sample of a solid mixture result from differences in size and lack of uniformity in the distribution of the different constituents, and from differences in the hardness and the specific gravity of these constituents. The general method of procedure in sampling a non-homogeneous solid, whether it represents a carload or a few pounds is essentially the same. It involves removing and setting aside according to a uniform plan a fractional part of the total amount, reducing the portion set aside to a finer state of division, mixing thoroughly, and repeating this cycle of operations until a sample of such fineness is obtained that the small amount actually weighed out represents the entire original mass. The fundamental principle which must be kept in mind is that the fineness to which the sample is crushed at each cycle must be such that the ratio between the size of the sample and the size of the largest particle is sufficiently large. The size of the largest particle must be so small that the addition of one such particle to the portion which has been selected does not change the average composition of the mixture by an appreciable amount.

Calculation of the Maximum Size of Particle. The maximum size of particle which is permissible depends upon a number of factors, and can be calculated if certain assumptions are made. The method is most conveniently outlined by the consideration of a specific case.

Let it be assumed that a lump of iron ore, which weighs 1000 gm., consists of 200 gm. of quartz, which has a specific gravity of 2.5 and contains no iron, and 800 gm. of hematite, which has a specific gravity of 4.5 and contains 60 per cent of iron. Let it be assumed further that it is desired to crush this lump to such a degree of fineness that when one-fourth of the well-mixed mass is selected the addition of a further particle of quartz will not reduce the percentage of iron, or of a further particle of hematite will not increase the percentage of iron, by more than one-tenth of one per cent. The correct percentage of iron in the lump is evidently 48, and if x and x' represent the respective weights of quartz and hematite whose size is just sufficient to meet the requirements named, the following expressions are true:

$$48 - \frac{(250 \times 48) + (x \times 0)}{250 + x} = 0.1,$$

$$\frac{(250 \times 48) + (x' \times 60)}{250 + x'} - 48 = 0.1.$$

When these expressions are solved x will be found to have the value 0.52 gm. and x' 2.1 gm. The volume of a quartz particle which weighs 0.52 gm. is evidently 0.208 cc. and if it is assumed to have the form of a perfect cube its length would be approximately 0.6 cm. The volume of a hematite particle which weighs 2.1 gm. is evidently 0.46 cc. and if it is also assumed to be a cube, its length would be 0.77 cm. Hence the sample should be crushed fine enough to pass thru a sieve which has openings not exceeding 0.6 cm. in diameter, and since the assumptions here made are not actually realized, a sieve with still smaller openings should be used if the specified degree of accuracy in the preparation of the sample is to be assured.

Methods of Selection. The simplest method of selecting a fractional part of the mixture is to turn over the entire mass with a shovel or spoon, and set aside every tenth, fifth, or second shovel or spoonful. Another method is to distribute the entire mass in the form of a cone-shaped pile, flatten the pile slightly, and remove a sector representing one-quarter or one-half of the pile; it can be assumed that the large and small particles and the light and heavy particles are distributed symmetrically with respect to the central axis of such a cone. A large number of mechanical devices, which automatically separate a fractional part of all the material passed through them, are used where the sample is large.

Methods of Powdering. A great variety of grinding or shredding machines, which are especially adapted to the nature of different classes of materials, are in use. Altho the grinding parts of such machines are made of hardened steel, appreciable amounts of iron are added to the sample during the grinding process if the sample contains constituents whose hardness approaches that of steel. This is usually neglected in commercial work, but cannot be tolerated in many lines of scientific work. In such cases the sample must be pulverized by hand by means of a mortar and pestle which are made of agate. It is sometimes advantageous to separate out the coarse from the fine particles during the grinding process; but since certain constituents of the mixture may be more easily reduced than others, none of the sample can be rejected, that is, the entire sample must be made to pass thru the sieve used.

Methods of Mixing. Mixing is best performed by placing the mass in a cylindrical vessel, which is then carefully corked and rotated by means of a motor. The same result can be obtained more slowly by hand rotation. Another method consists in placing the sample on a large piece of rubber "sampling-cloth" and rolling the contents toward the center by raising successively the opposite corners of the cloth. Mixing and grinding can be effected simultaneously by means of the small "ball mill" repre-

sented in Fig. 5. It consists of a porcelain jar, which contains in addition to the sample a large number of porcelain balls. When closed and rotated these rapidly reduce the sample to a fine homogeneous mixture.

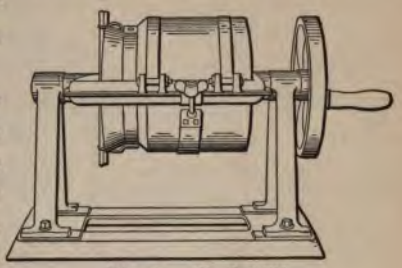

Fig. 5. — Ball Mill

The Moisture Content of the Sample. All solid substances contain at least appreciable amounts of hygroscopic water unless previously dried. If the percentage is large the fine particles tend to stick together and may make it impossible to powder and mix the sample properly. Frequently a mass which seems to be fairly dry becomes moist and sticky as soon as it is roughly powdered, since water is sometimes held within the interior of the larger masses.

The chemist is usually expected to report results on the basis of the mixture actually received. If he dries the mixture submitted to him in order to make it possible to prepare a representative sample the results obtained will not represent the composition of the original mixture. In such cases it becomes necessary to save out a sufficient amount of the original mixture to permit of an accurate determination of the water present, and to multiply the results of the analysis by a factor, which can be calculated from the percentage of water found, in order to report the percentages present in the original mixture.

If the sample contains a small amount of hygroscopic water only it is preferable not to dry it, for since all finely divided substances are at least appreciably hygroscopic it is often difficult to preserve such samples and to weigh them out accurately.

Methods of Drying. Hygroscopic water is usually determined by drying the sample in an oven (see Chapter IX) which is kept at a temperature of 105°. This method cannot be used where the sample loses chemically combined water, or undergoes other

changes at this temperature. In such cases, dehydration can be effected by the use of a desiccator similar to the one represented in Fig. 6. It consists of a glass vessel provided with a tightly fitting cover, and containing some substance, such as strong sulfuric acid or calcium chloride, which is a good absorbent of water. The general theory of its use will be discussed in Chapter X.

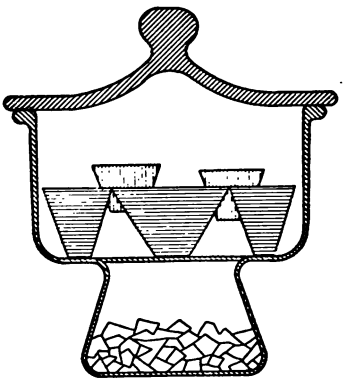

Fig. 6. — Desiccator

Still another device which sometimes becomes necessary is to absorb the water by means of a filter paper or a porous plate. The finely powdered substance is manipulated by means of a spatula in such a manner that fresh portions of the mass are constantly brought into contact with the plate or paper; the capillary action of these agents gradually absorbs the adhering water.

CHAPTER IV

THE PROPERTIES OF SOLUTIONS AND THE ELECTROLYTIC DISSOCIATION THEORY

The Possible Kinds of Solutions. Solutions are defined as homogeneous mixtures whose composition can undergo continuous variation between certain definite limits. Such mixtures representing all three states of aggregation are known. All substances in the gaseous state are miscible with each other in any proportions whatever. In the liquid state the possibilities are limited; certain pairs of liquids, such as alcohol and water, are capable of forming a continuous series of homogeneous mixtures; others, such as ether and water, are mutually miscible to a limited extent only. In the solid state the possibilities are still more limited and it was only comparatively recently that the existence of "solid solutions" was recognized. Instances in which two solids are miscible in any proportions whatever are known, but usually solids are soluble in each other to a limited extent only. Solids which are closely related to each other crystallographically, that is, which are isomorphous, usually form solid solutions with one another. Many solid mixtures which appear to be homogeneous can be shown by examination with a microscope to be very finely-grained conglomerates of the constituent solids, and, therefore, are not true solutions.

Substances existing in different states of aggregation are often able to form solutions with each other. Gases are frequently soluble in both liquids and solids up to a certain extent; liquids sometimes dissolve in solids to a limited extent, and solids are often soluble in liquids. In dealing with solutions of all classes it is customary to designate the substance present in relatively large amount as the "solvent" and the substance present in relatively

small amount as the dissolved substance or "solute." If the two constituents of the solution are miscible in all proportions either may be the solvent or the solute according to the proportions represented in the mixture concerned.

Solutions of Gases in Liquids. The solubility of a gas in a liquid is usually expressed in terms of the volume of gas, measured under standard conditions of temperature and pressure, dissolved by a unit volume of the liquid. The gases which are most frequently dealt with in quantitative work are, with the exception of ammonia and the halogen acids, but slightly soluble in water, or aqueous solutions which do not act upon the gas chemically. With one or two exceptions only, the solubility of a gas in a liquid is decreased by increasing the temperature. The amount of gas dissolved by a liquid increases in direct proportion to the pressure of that gas in contact with the liquid except in those cases in which the solubility is very great. The complete saturation of a liquid with a gas requires intimate contact of the two components for some time, and is not usually attained unless a stream of gas is permitted to pass through the liquid, or unless the liquid is shaken with an excess of the gas in a closed vessel.

Solutions of Solids in Liquids. The solubility of a solid in a liquid is expressed either in terms of the number of grams of solid which can be dissolved in a liter of the pure liquid, or of the number of grams of solute present in a liter of the saturated solution. The weight of solute present in a unit volume of any solution, whether saturated or not, is known as the "concentration." Increasing the temperature usually increases the solubility of solids in liquids, altho the increment per degree is often small; a relatively small number of cases are known in which the solubility decreases with increasing temperature. The effect of pressure upon the solubility of solids is small and unless the differences concerned amount to a hundred atmospheres can be neglected.

The Speed of Solution of Solids in Liquids. The rate at which a solid dissolves in a liquid depends primarily upon the rate

at which the particles of solid are taken up by the liquid, and the rate at which the dissolved particles pass away from the immediate neighborhood of the solid and diffuse into the surrounding liquid. Both of these factors depend upon the specific natures of the solid and liquid concerned, and upon the temperature and concentration of the solution with respect to the dissolved salt. Increasing the temperature increases both the rate at which the solid body is taken up and the rate at which the dissolved particles diffuse into the surrounding liquid. The rate of diffusion is further directly proportional to the difference between the concentration of the solution with respect to the dissolved salt at any two points in the solution. Further, the amount of surface of the solid as compared with the volume of liquid to be saturated and the rate at which the concentrations of different portions of the solution are equalized thru mechanical agencies greatly affect the rate at which saturation of the solution is effected.

It is apparent that wherever it is desired to dissolve a given amount of solid rapidly the latter should be reduced to a fine state of division in order that the extent of surface presented shall be as large as possible, that the temperature be as high as the other conditions of the experiment permit, and that the solid and liquid be agitated violently.

Supersaturated Solutions. Altho the rate at which a solid is dissolved by a liquid decreases as the concentration of the resulting solution increases, and becomes zero as soon as the solution has attained a certain maximum concentration, it is possible, under certain conditions, to prepare solutions which contain more than the normal quantity of dissolved solute; such solutions are then designated as "supersaturated." Supersaturated solutions usually result when a solvent is saturated with a solute at a temperature at which the solubility is greater and the temperature slowly changed to that at which the solubility is less; or, where the solid is generated in the solvent as the result of changes in the composition of the liquid. The excess of dissolved

solute usually separates out from such solutions on standing, especially if the mixture is agitated.

Effect of Size of Particles on Solubility of Solids. The size of the solid particles in contact with the solvent affects not only the rate at which the solid dissolves but, in some cases at least, affects the actual value of the solubility constant. This was clearly shown through a series of experiments* on the solubility of gypsum ($CaSO_4 \cdot 2\,H_2O$) and barium sulphate in water. Solutions which had been thoroughly saturated thru long contact with particles of gypsum of moderate size were found to show a decided increase in concentration as soon as a small amount of more finely divided particles were added; on long standing, however, the very fine particles all disappeared, and the solubility constant attained its former magnitude. Solutions saturated with particles whose average diameter was 0.002 mm. were found to contain 2.085 gm. of calcium sulfate per liter; if saturated with particles whose average diameter was 0.0003 mm. the concentration corresponded to 2.476 gm. per liter, that is, decreasing the size of the solid particles from 0.002 to 0.0003 mm. increased the solubility by about nineteen per cent. Further experiments showed that with solid particles whose average diameters equaled or exceeded 0.002 mm. the solubility value remained constant and was therefore designated as the "normal solubility"; if the particles concerned were less than 0.002 mm. in diameter the solubility value exceeded the normal but gradually attained the normal value, and the very fine particles gradually disappeared. Experiments with barium sulfate gave still more striking results. When precipitated from a boiling solution the particles of salt showed an average diameter of 0.0018 mm. and gave a normal solubility of 0.0023 gm. per liter; when the particles of precipitate were reduced to 0.0001 mm. the solubility was increased to 0.00415 gm. per liter and with the naturally occurring salt, reduced to a still finer state of division, the solubility reached 0.00618 gm. per liter.

* Hulett, Zeitschrift für physikalische Chemie, **37**, 385 (1901).

These facts explain the well-known phenomenon that particles of a precipitate which are too small to be retained by a filter are often retained on the same filter after they have been allowed to remain in contact with the solution for some time. It is probable that there is a tendency for all finely divided substances in contact with their saturated solutions to increase the size of their particles up to a certain maximum, and for the resulting saturated solutions to attain a certain normal solubility. If this is generally true all solutions which have been saturated with a solid, some of the particles of which are below the normal size, are supersaturated with respect to the particles which exceed the normal size, and on standing some of the dissolved substance should be deposited upon these large particles; further, since the solution would then be undersaturated with respect to those particles which are smaller than the normal size, these should pass into solution. The total effect should be the gradual disappearance of all particles whose size is below the normal. Changes of this kind are found to take place much more rapidly as the temperature of the mixture is increased.

The Molecular Weights of Dissolved Substances. It was first shown by Van't Hoff in 1886 that a remarkable analogy exists between dissolved and gaseous substances. He was able to show from the data available at that time that the "osmotic pressure"* exerted by a substance dissolved in a liquid was directly proportional to the concentration and to the absolute temperature; further, that the osmotic pressure of such a solution was exactly equal to the gaseous pressure which the solute should exert, if it was vaporized, and if the vapor occupied a space equal to the volume of the solution concerned. The validity of these conclusions has been tested by more recent investigators, and so far

* The student should consult some modern book on Theoretical Chemistry, or the first volume of Stieglitz' "Qualitative Analysis," for an explanation of this term and for a further elaboration of much of the matter which follows.

as solutions of small concentration are concerned, sufficiently confirmed. They render it almost necessary to assume that the hypothesis of Avogadro is as valid for dissolved substances as for gases, and hence Van't Hoff was led finally to the conclusion that equal volumes of solutions of different substances, which give equal osmotic pressures, at the same temperature, contain the same number of molecules.

The most important application of these conclusions was the calculation of the molecular weights of dissolved substances from determinations of the osmotic pressures of solutions containing them. Owing to the practical difficulties which arise in the determination of osmotic pressures, certain physical properties which are related to osmotic pressure, such as the changes in the vapor pressure of the solvent, and in the boiling or freezing point of the solution, have been more generally used for the determination of the molecular weights of dissolved substances. When these methods were applied to certain classes of solutions, especially to dilute aqueous solutions of strong acids, of strong bases, and of salts in general, the molecular weights obtained were less than the values usually assigned to these substances, in many cases approximately one-half or one-third of these values. Van't Hoff was unable to explain these discrepancies.

Development of the Electrolytic Dissociation Theory. In 1887 Arrhenius noted the fact that when osmotic pressure methods were used for the determination of molecular weights, normal values were obtained for those solutions which did not conduct electricity, whereas abnormally low results were obtained with all solutions which were good conductors. It had been already shown by Faraday that the passage of an electric current through a solution was always associated with the decomposition of the solute into two products, one of which separated at the negative pole or cathode, and the other at the positive pole or anode; and further, that the amount of electricity transmitted was directly proportional to the weights of either of the decomposition products

formed. These facts suggested to Arrhenius the "Electrolytic Dissociation Theory."

According to this theory all substances which form solutions capable of conducting an electric current, and, therefore, designated as "electrolytes," do not exist in such solutions in the form of the original molecules, but in part at least as "dissociation products." These products are designated as "ions," or more specifically as "cations" or "anions," according to whether they separate at the cathode or anode during the passage of an electric current through the solution. The ions are either simple elements or combinations of elements charged with large amounts of electricity, each cation with a definite amount of positive electricity, and each anion with an equal amount of negative electricity, or with some simple multiple of that amount.

According to these assumptions the abnormally low results obtained for the molecular weights of electrolytes is a necessary consequence of the fact that such solutions contain a greater number of ultimate particles, that is ions, capable of affecting the osmotic pressure of the solution than would be present if the solution was undissociated. Such solutions are conductors because the positively charged cations are attracted by the negatively charged cathode and repelled by the positively charged anode, while the negatively charged anions are attracted by the positively charged anode and repelled by the negatively charged cathode. These attractions and repulsions cause the cations to migrate toward the cathode, and the anions toward the anode, that is, cause a flow of electricity through the solution. When the ions reach the surfaces of the electrodes they lose their charges, which change materially affects their chemical and physical properties, and is the cause of the phenomenon of "electrolysis."

Composition of the Ions. The probable composition of the ions which are present in a solution of an electrolyte can usually be inferred from the composition of the substances which separate at the electrodes during electrolysis. When a solution of hyd-

chloric acid is electrolyzed gaseous hydrogen separates at the cathode and chlorine at the anode. The simplest assumption which can be made is that such a solution contains positively charged hydrogen ions and negatively charged chlorine ions; the hydrogen atoms, which result from the loss of positive charges by two hydrogen ions, unite to form a molecule of hydrogen, and the chlorine atoms, which result from the loss of negative charges by two chlorine ions, unite to form a molecule of chlorine. Since solutions of all soluble chlorides yield chlorine during electrolysis it is probable that all such solutions contain simple chlorine ions. When a solution of a strong base, such as potassium hydroxide, is electrolyzed hydrogen is liberated at the cathode and oxygen at the anode. It is probable that the solution contains positively charged potassium ions and negatively charged ions having the formula HO. The metallic potassium which first separates at the cathode at once reacts with water to form hydrogen and more potassium hydroxide; the negatively charged HO ions cannot exist independent of this charge, and unite to form water and molecular oxygen. All hydroxides yield solutions containing these ions. When a solution of copper sulfate is electrolyzed, metallic copper separates at the cathode, and oxygen at the anode and the solution becomes acid. It seems probable that the solution contains positively charged copper ions and negatively charged ions of the formula SO_4; the former yield metallic copper at the cathode, but as the latter cannot exist independent of their negative charge they decompose and unite with water, forming oxygen and sulfuric acid, which in turn gives hydrogen ions and SO_4 ions.

A more careful study of the subject, by methods which need not be considered here, shows that the dissociation of even simple electrolytes may be a more complex process than the foregoing statements suggest. It is known, for example, that solutions of sulfates contain ions of the formula HSO_4, in addition to SO_4 ions, also that phosphates yield ions of the formula H_2PO_4, HPO_4 and PO_4. Further, certain metallic ions show a decided tendency to

unite with other groups of elements such as H_2O, NH_3, Cl_2 and $(CN)_2$.

In order to designate the various ions, symbols which represent not only their chemical composition but also the number and character of the charges which they carry are used. The charge carried by the hydrogen ion is chosen as the standard of comparison and represented by a single + sign written above the symbol, ions which carry double this amount of positive charge are represented by the proper symbol with the + sign written twice. Similarly, ions which carry negative charges equal to the positive charge of the hydrogen ion are represented by the proper symbol with a single − sign written above it, those which carry twice this amount of charge show the − sign written twice.

Factors Affecting the Dissociation of Electrolytes. Since electricity is carried through a solution by the ions, not by the undissociated molecules which it contains, its "conductivity," that is its efficiency as a conductor, is a measure of the extent to which the electrolyte is dissociated. In comparing the conductivities of solutions, the relations are greatly simplified if concentrations are expressed in terms of gram molecules or "moles" per liter, that is, if the weight of solute per liter is divided by the molecular weight of the solute concerned.

When the conductivities of solutions, which contain the same number of moles of various electrolytes per liter, are measured in the same apparatus and under identical conditions very different values are obtained. These differences have been shown to be due in part to variations in the speed with which the different ions travel when attracted by a charge of the same intensity, and in part to the fact that the different electrolytes are not dissociated to the same extent.

When the conductivities of solutions containing different concentrations of the same electrolyte are measured under identical conditions, and the results are divided by the respective concentrations it is found that the quotients obtained for the weaker solu-

tions exceed those obtained for the stronger solutions. This seems to mean that the percentage of electrolyte which exists in the dissociated condition is greater in dilute than in concentrated solutions. It has been shown, however, that altho the conductivities of all electrolytes increase as the concentration of the solution decreases, the conductivity attains a definite limiting value at a certain concentration which is not changed by further dilution. It seems probable that this limit, corresponding to the so-called "maximum conductivity," represents the conductivity of the completely dissociated electrolyte. If this conclusion is accepted the ratio between the conductivity of a solution of any electrolyte and the maximum conductivity of that electrolyte is a measure of the "degree of dissociation" of the electrolyte in the solution concerned.

Extent to Which Different Electrolytes are Dissociated. Some of the results, showing the extent to which solutions containing different concentrations of a number of electrolytes are dissociated, which were obtained by the method just outlined, are given in the accompanying table.* The first column gives the concentrations in moles per liter, the remaining columns the percentage of dissociation of the given reagents at different concentrations. It is now known that the method here used gives results which are only rough approximations of the correct values for solutions whose concentrations exceed molar, probably owing to the resistance offered by large concentrations of non-ionized molecules.

The differences between the percentages given for strong acids like nitric, hydrochloric, and sulfuric and a weak acid like acetic are striking, even where the concentrations are below molar. Similar differences are shown between the figures for a strong base like potassium hydroxide, and a weak base like ammonium hydroxide. They are found to be characteristic of all acids and bases and there is abundant evidence for the statement that what is com-

* From data of Kohlrausch and Holborn, Leitvermögen der Electrolyte, 160.

Conc.	HCl	HNO_3	H_2SO_4	$H(C_2H_3O_2)$	NaCl	KOH	$(NH_4)OH$
10	17.08	17.44	19.02	0.05	.....	19.14	0.08
7	28.17	28.53	28.67	0.14	.....	33.00	0.17
5	40.37	40.16	36.68	0.27	38.92	45.21	0.31
4	48.14	49.60	41.14	0.36	44.84	52.22	0.40
3	57.03	58.66	45.32	0.50	51.50	60.08	0.55
2	67.37	68.80	49.73	0.75	59.07	68.72	0.80
1	79.84	82.66	53.00	1.23	67.82	78.63	1.35
0.5	86.74	86.40	55.71	1.87	73.74	84.19	2.06
0.1	93.10	93.33	61.14	4.30	84.32	91.02	5

monly known as the "strength" of an acid or base depends upon the extent to which it is dissociated at different concentrations.

The table shows further, that sodium chloride resembles the strong acids and bases rather than weak ones, and a large amount of experimental work is available which shows that most salts, with the exception of mercuric cyanide and certain other salts of mercury and cadmium, are largely dissociated.

It has also been shown that water possesses the property of causing solutes to dissociate to a greater extent than any other solvent; alcohol possesses this property to some extent, but the remaining organic solvents yield solutions which are non-conductors.

Importance of the Electrolytic Dissociation Theory. This theory is of especial importance in the study of quantitative analysis owing to the fact that many of the chemical reactions upon which quantitative processes are based are reactions between electrolytes, and there are decided differences between reactions of this type and those in which electrolytic dissociation plays no part. In general, the ions possess a much greater chemical activity than undissociated molecules, and the extent to which two reagents react with each other, and the speed with which they react is often largely determined by the extent to which these reagents or the products which result from their interaction are dissociated.

The theory enables us to understand a large number of facts which are difficult to explain on any other basis, and to predict with a fair degree of certainty many effects which can be used to advantage in analytical chemistry.

CHAPTER V

THE FACTORS WHICH DETERMINE CHEMICAL EQUILIBRIUM

Equilibrium and Reaction Velocity. When two substances react chemically they are in a condition of unstable equilibrium with respect to each other; when no further changes in the relative masses of these substances are taking place, "equilibrium" has been reached. This condition is also defined by the statement that the "reaction velocity" is zero, where the term reaction velocity is defined as the mass of one or both of the original substances transformed into new substances during some unit of time. The velocity of many chemical reactions, especially those designated as "explosive" must be expressed by very large numbers, even when the unit of time adopted is the second; that of other reactions is so small that the day is the more convenient unit to employ. Most of the reactions which are of importance in quantitative analysis have velocities which are too great to be determined with even approximate accuracy.

Homogeneous and Heterogeneous Equilibrium. In discussing the subject of chemical equilibrium and reaction velocity a very important factor to be considered is whether all the reacting substances, and all of the products of the reaction, exist in the same phase and the nature of this phase. (For a definition of the term phase see page 3.) If all the substances concerned are gases, or if all remain dissolved in the same liquid phase thruout the reaction period, their respective concentrations remain uniformly distributed thruout the entire mass, and the resulting equilibrium is called "homogeneous." If the reacting substances exist as two distinct phases, or if two distinct phases result as the reaction progresses, the resulting equilibrium is called "hetero-

geneous." In homogeneous equilibrium the reaction velocity is uniform at all points thruout the reacting mass; in heterogeneous equilibrium the reaction velocity may differ in the different phases, and may be reduced to practically zero except at the surfaces of contact between the different phases.

A condition of perfect equilibrium between the different phases of a heterogeneous system must result if they are allowed to remain in contact for a sufficient length of time, but the extent of the surfaces of contact between these phases and the rates at which the products of the reaction diffuse away from the immediate neighborhood of these surfaces materially affect the time needed for the establishment of this equilibrium.

Factors Affecting Chemical Equilibrium. There are four factors which materially affect the direction and rate of progress of chemical reactions: first, the chemical properties of the reacting substances; second, the concentrations of the substances taking part in the reaction; third, the temperature; and fourth, the pressure.

As regards the first of these factors our present knowledge suggests the theory that among the other specific properties with which every substance is endowed is a certain intensity of chemical energy or chemical potential, and in general, any two substances tend to react with each other to an extent directly dependent upon the difference between the intensity of the chemical energy associated with them. In other words, there is a universal tendency for the equalization of chemical intensities just as there is a universal tendency for the equalization of heat intensities, and no reaction takes place which does not involve a reduction in the chemical potential of the mixture.

The action of the second factor is expressed in the "Law of Mass Action," which states that the speed of the reaction between any two substances in a mixture is proportional to the product of the concentrations of these substances in that mixture, where the concentrations are expressed in moles per unit volume. According

to this law the expression for a reaction between the substances A and B which unite to form the substances P and Q is

$$(C_A)^a \cdot (C_B)^b \cdot k = (C_P)^p \cdot (C_Q)^q \cdot k'.$$

In this expression (C_A), etc., represent the concentrations of these molecules; a, b, etc., the number of molecules of these substances concerned in the reaction; k a constant representing the speed of the reaction between A and B; and k' a constant representing the speed of the reaction between P and Q. Since k and k' are both constants the expression can be simplified by dividing by k' and substituting K for $k \div k'$; it then becomes

$$K = \frac{(C_P)^p \cdot (C_Q)^q}{(C_A)^a \cdot (C_B)^b}.$$

It might have been simplified by dividing by k, in which case $k' \div k$ or K would have a value represented by the reciprocal of that given in the above expression. Thruout this book the former procedure will be employed, that is, where K is referred to, it should be understood to represent the constant obtained when K appears on the left of the sign of equality in the mass law expression.

It is evident that K represents a ratio, whose value depends on the specific properties of the four substances A, B, P and Q, and not upon the concentration in which any one or two of them exist in the mixture. If a mixture is made in which $(C_P)^p \cdot (C_Q)^q \div (C_A)^a \cdot (C_B)^b$ exceeds K, (C_A) and (C_B) must increase, and (C_P) and (C_Q) must decrease until the mass law expression is satisfied, that is, the reaction must progress from right to left. If this quotient is less than K the reaction must progress from left to right. In general, if the value of K is large the predominating tendency is for the reaction to proceed from left to right; if it is a small fraction of unity the predominating tendency is for it to progress from right to left. Since the value of K determines to a large extent the direction in which reactions progress it is called the "reaction constant" or "equilibrium constant."

The effect of temperature upon a reaction depends upon whether it absorbs or liberates heat. Increasing the temperature displaces the equilibrium in the direction of that reaction which absorbs heat, that is, it increases K if heat is absorbed when the reaction progresses from left to right; it displaces equilibrium in the reverse direction if heat is given out, that is, it decreases K if heat is liberated when the reaction progresses from left to right.

The effect of pressure upon a reaction depends upon whether the volume of the reacting mass is increased or decreased as the reaction progresses. If it is decreased, increasing the pressure favors the reaction, and increases the value of K; if it is increased it inhibits the reaction and decreases the value of K. The volume changes in reactions in which only solid and liquid phases are concerned are so small that they have an inappreciable effect upon the value of K. When gases are produced or absorbed as the reaction progresses pressure has a large effect upon the value of K.

An Illustration of Homogeneous Equilibrium. The manner in which the factors named in the preceding section affect a simple reaction involving homogeneous equilibrium can be most easily comprehended by considering a specific case, such as the action between acetic acid and ethyl alcohol. These substances as well as the products of their interaction are soluble in each other to an unlimited extent. When acetic acid is added to alcohol the resulting reaction is represented by

$$(C_2H_5)HO + (CH_3)COOH \rightarrow (C_2H_5)COO(CH_3) + H_2O.$$

If water is added to ethyl acetate, alcohol and acetic acid are produced, that is, the reaction progresses in the reverse direction when the concentrations of water and ethyl acetate are large. If either of the two mixtures are allowed to stand until equilibrium has been attained the concentrations of the four substances in the mixture must be in accord with the expression

$$K = \frac{(C_4H_8O_2) \cdot (H_2O)}{(C_2H_4O_2) \cdot (C_2H_6O)},$$

in which, and in all of the subsequent pages of this book, a chemical formula enclosed in brackets designates concentrations of the corresponding substance expressed in moles per liter. The value of K in this expression has been found to be 4 and it is easy to calculate the composition of the mixture which results when known quantities of alcohol and acetic acid or of ethyl acetate and water are mixed. Suppose we make a mixture of 240 gm. of acetic acid, 138 of alcohol and 54 of water. If we represent the volume of the mixture before any action takes place by V then ($C_2H_4O_2$) in that mixture is $240 \div 60\ V$ or $4 \div V$, (C_2H_6O) is $138 \div 46\ V$ or $3 \div V$ and (H_2O) is $54 \div 18\ V$ or $3 \div V$.

If x represents the moles of ethyl acetate present after equilibrium has been attained, x also represents the moles of water produced by the reaction, also $(4 - x)$ the moles of acetic acid and $(3 - x)$ the moles of alcohol left uncombined. If we represent the final volume of the mixture by V' the mass law expression becomes

$$\frac{4-x}{V'} \cdot \frac{3-x}{V'} \cdot 4 = \frac{x}{V'} \cdot \frac{3+x}{V'},$$

from which $48 - 28x + 4x^2 = 3x + x^2$.

When solved for x the latter is found to have the value 1.9 which means that the final mixture contains 1.9×88 or 167.2 gm. of ethyl acetate and $54 + (1.9 \times 18)$ or 88.2 gm. of water.

Since the formation of ethyl acetate and water liberates heat, increasing the temperature decreases the value of K and decreases the amount of ethyl acetate and water produced.

Since no gases are either produced or absorbed, pressure has no appreciable effect upon the value of K and does not affect the amount of ethyl acetate and water formed.

Reversible and Irreversible Reactions. In the reaction discussed in the previous section the constant K has a moderately large value; this means that altho the tendency for the reaction to progress in one direction preponderates over its tendency to progress in the reverse direction, both tendencies are recognizable,

and where equivalent concentrations of the reacting substances are used, large concentrations of all four substances are present in the resulting mixture. Such reactions are spoken of as "reversible."

In many reactions, however, the value of the constant K is either very large or small; this means that the tendency for the reaction to progress in one direction greatly preponderates over the reverse tendency, and with equivalent concentrations of the reacting constituents, conversion into the resulting products is practically complete. Such reactions are spoken of as "irreversible," altho strictly speaking, all reactions are to be regarded as reversible to some degree even tho it may be difficult to recognize the fact experimentally. Most quantitative processes which depend upon the employment of chemical reactions are inaccurate unless the substance under treatment is almost completely transformed into the desired compound, and reactions whose constants are large are the only ones which can be employed to advantage in such processes. The factors already discussed may be used to assist in displacing the equilibrium of reversible reactions in the desired direction.

Reactions Involving Heterogeneous Equilibrium. The factors which affect chemical reactions also affect the processes of evaporation and solution, and the simplest illustrations of heterogeneous equilibrium are those in which two phases containing different concentrations of the same substance are in equilibrium with each other. This is true of a solid or liquid which is in equilibrium with its vapor, or of a solid which is in equilibrium with a solution. All such systems conform to a very simple law, namely, that the ratio between the concentrations of the substance concerned in the two phases is constant for any given temperature. When, for example, a solid substance is brought into contact with a liquid it continues to dissolve until the solution is saturated, that is, when equilibrium between the two phases has been attained the solution contains a fixed concentration of the dissolved substance, and since the

solid phase represents the pure substance its concentration does not vary, but depends only upon its specific gravity. Hence the general expression for the equilibrium condition becomes

$$K = C,$$

in which C represents the concentration of the saturated solution. The more complex examples of heterogeneous equilibrium will be discussed in Chapters X, XVI and XXXII.

Reaction Velocity and Catalysis. The speed with which a reaction progresses depends upon the specific properties of the reacting substances and their concentrations; in general, it is more than doubled for every increase of 10° in the temperature of the reacting mass.

The reaction velocity of certain processes is increased in an abnormal manner by certain substances and decreased by others. The former class of substances are known as positive — and the latter as negative — catalyzers. Very small concentrations of a catalyzer may produce very marked effects, and as they do not suffer an appreciable change in concentration they must act indirectly, that is, form one or more intermediate compounds with the reacting substances which at once decompose into the original catalyzer and the desired end product. According to this theory the velocity of the reaction is increased because the velocities of the intermediate reactions greatly exceed that of the direct reaction between the original substances. They have no effect upon the value of the equilibrium constant, but increase the speed at which a condition of equilibrium is attained.

CHAPTER VI

THE CHEMICAL ACTIVITY OF ELECTROLYTES

Preliminary Statements. In outlining the general principles which determine reaction velocity and equilibrium in the previous chapter the possibility of electrolytic dissociation was not considered. The principles there set forth are universally valid, and if the dissociation theory is also accepted it becomes necessary to point out how these principles should be applied to the study of reactions between electrolytes. Since, according to this theory, the ions possess a greater chemical activity than the original molecules, the concentrations of the ions should determine the reaction velocity and the resulting equilibrium, to a greater extent than the concentration of the original molecules. Experience confirms this suggestion, for a great variety of well-established facts show that the chemical properties of solutions of largely dissociated electrolytes can be most easily understood by assuming that these properties depend upon the concentrations of the ions which they contain.

The Law of Electro-neutrality. Whenever a compound undergoes electrolytic dissociation the quantity of positive electricity, which is associated with the resulting cations, exactly equals the quantity of negative electricity, which is associated with the resulting anions, and the solution obtained is, therefore, electrically neutral. The quantity of positive charge which is associated with the hydrogen ion is fixed and invariable; all other cations bear positive charges, which are either equal to, or simple multiples of, this charge; all anions bear negative charges which are either equivalent to the positive charge associated with the hydrogen ion,

or to simple multiples of it. The value of these multiples is determined in all cases by the valence of the element, or the combination of elements representing the composition of the ion, in the undissociated molecule. Those elements which form compounds representing different degrees of oxidation also form ions associated with different amounts of electrical charge, and the properties of such ions depend upon the charges with which they are associated. Thus the cation which results from the dissociation of a ferrous salt differs from the cation resulting from the dissociation of a ferric salt, in that the former consists of an iron atom associated with two positive charges, the latter of an iron atom associated with three positive charges.

When solutions containing different electrolytes are brought together various changes may take place. Certain ions which possess but slight affinity for their charges may give them up to other elements or groups of elements and form more stable ions. Certain di- or tri-valent ions may lose a half or a third of their charges, or certain uni- or di-valent ions may take up charges and become di- or tri-valent. In other instances certain charges may disappear entirely from the solution. The law of electro-neutrality requires that, whatever the character or complexity of these changes, the solutions must remain electrically neutral; that is, wherever positive charges disappear, an equivalent number of negative charges must disappear simultaneously; and wherever positive charges are added to the solution, equivalent amounts of negative charges must be added to it at the same time.

The Chemical Activity of Acids. All acids which dissociate to an appreciable extent, produce corresponding concentrations of hydrogen ions, and the characteristic properties of aqueous solutions of this class of substances are dependent upon this fact. In so far as these general properties are concerned, the element or combination of elements with which the hydrogen is combined in the undissociated molecule is of importance mainly in that it determines the extent to which the acid undergoes dissociation

when dissolved in water. Thus the chlorine atom possesses a greater affinity for a negative charge than the $C_2H_3O_2$ group, hence the sum of the forces which tend to bring about dissociation of the hydrochloric acid molecule will exceed the sum of the forces which tend to bring about dissociation of the acetic acid molecule; since solutions of both acids must remain electrically neutral, the concentration of the hydrogen ions in a solution of hydrochloric acid must exceed the concentration of the hydrogen ions in solutions of acetic acid of equivalent concentration.

The chemical activity of an acid can be measured by determining the rate at which solutions containing known concentrations of the acid in question affect certain chemical transformations. The chemical activities of solutions containing equivalent amounts of some of the more important acids have been determined by a variety of methods, and the differences in the values thus obtained are found to agree at least approximately with the corresponding variations in the concentrations of the hydrogen ion present, as calculated by the method described on page 40. The conductivity of an aqueous solution of an acid containing one equivalent in grams per liter is, therefore, a measure of its "strength." The comparative conductivities of some of the more important acids are given in the following table in which the conductivity of hydrochloric acid has been arbitrarily given the value of 100.

Hydrochloric acid	100
Hydrobromic acid	104
Nitric acid	99.6
Sulfuric acid	66.4
Oxalic acid	19.7
Phosphoric acid	7.27
Arsenic acid	5.38
Formic acid	1.68
Acetic acid	0.42
Succinic acid	0.58
Tri-chlor acetic acid	62.3

These numbers relate to normal concentrations only, and increasing or decreasing the concentration does not increase or decrease the conductivity, and, therefore, the strength of the solution to

a corresponding degree. The concentration of the hydrogen ion present in any solution of an acid equals the product of the numbers representing the concentration of the acid, in gram equivalents per liter, and the degree of dissociation of the acid at that concentration. Since the degree of dissociation increases with the dilution the series of numbers given in the table should become more nearly equal with decreasing concentration. The highest attainable concentration of hydrogen ion is found in a solution of nitric acid having a specific gravity of 1.19; this solution contains about 31 per cent of HNO_3, of which about 35 per cent is dissociated, hence the concentration of hydrogen ion represented by such a solution is about 2 gm. per liter.

The non-acidic properties of solutions of acids are determined by the concentrations of the anions present, and, also, especially with those acids which are but slightly dissociated, upon the undissociated molecules, whose chemical activity cannot be entirely disregarded.

The Chemical Activity of Bases. All bases which dissociate to an appreciable extent produce corresponding concentrations of the hydroxyl (HO) ion, and this fact determines the characteristic properties of aqueous solutions of this class of substances. The extent to which different bases dissociate depends upon the nature of the cation to which they give rise, or more specifically upon the strength of the affinity of the cation for its positive charge. The chemical activities of solutions containing equivalent concentrations of different bases have been determined by methods similar to those used in the study of acids. The results show a substantial agreement between the chemical activity and the degree of dissociation, that is the "strength" of a base is determined by the concentration of the hydroxyl ion which results when it is dissolved in water. The comparative conductivities of fortieth normal solutions of some of the more common bases are represented by the numbers of the following table, in which the number 100 has been arbitrarily assigned to potassium hydroxide.

Potassium hydroxide	100
Sodium hydroxide	92
Lithium hydroxide	88.2
Ethyl amine	12.46
Ammonium hydroxide	2.53

The Chemical Activity of Salts. The salts of most acids and bases are largely dissociated in aqueous solutions of moderate concentration, hence the concentrations of the anions or cations present in solutions containing equivalent concentrations of salts of the same acid or base are more nearly equal, and the chemical properties of such solutions are more nearly uniform. Certain salts, especially certain salts of mercury and cadmium are peculiar in that they ionize to a slight extent only, and as a consequence the reactions of these salts are somewhat anomalous. The phenomenon of "hydrolysis," which will be discussed in a succeeding section, is the cause of marked peculiarities in the chemical properties of certain salts.

Dissociation in Solutions Containing a Single Electrolyte. The dissociation of an electrolyte should obey the law of mass action. The general expression representing the dissociation of a molecule AB, which yields two ions A^+ and B^-, is:

$$(AB) \cdot k = (A^+) \cdot (B^-), \quad \text{or} \quad k = \frac{(A^+) \cdot (B^-)}{(AB)}.$$

The value of k in this expression depends upon the specific properties of the electrolyte and the temperature; it expresses the tendency of the electrolyte to undergo dissociation, and is generally known as the "dissociation constant."

It was noted in Chapter IV that the degree of dissociation of an electrolyte increases with the dilution, and an expression which represents the effect of dilution on dissociation can be derived from the mass law. If we represent the concentration of an electrolyte which dissociates into two ions by a and the fraction of it which is dissociated by x, ax must represent the concentration of both anion and cation and $(a - ax)$ that of the undissociated electrolyte. If

the volume of solution be represented by V the mass law expression is

$$(1)\ \frac{a-ax}{V}\cdot k=\frac{(ax)}{(V)}\cdot\frac{(ax)}{(V)},\qquad \text{or}\qquad (2)\ k=\frac{a(x)^2}{(1-x)V}.$$

This formula, which was first proposed by Ostwald, has been tested by determining the effect of dilution on the conductivity of a long series of electrolytes. When the value of k was calculated from these determinations it was found to be nearly constant for all the weaker acids and bases, but was found to decrease decidedly with dilution for the strong acid and bases, and for most salts. This means that the dissociation of those electrolytes which are largely dissociated does not increase with the dilution as much as the law of mass action demands. Several modifications of the expression designed to more accurately represent the effect of dilution on the dissociation of these electrolytes have been suggested; they all contain one or more empirically determined constants and need not be considered here.

The use of the expression given can be shown by a simple illustration. Let us suppose that we have two liters of a solution which contains 20 gm. of acetic acid and let us represent the fraction dissociated by x. Then the number of moles present if there were no dissociation would be $20 \div 60$, or 0.333, and both H^+ and $C_2H_3O_2^-$ are represented by $0.333\ x$, while $C_2H_4O_2$ is represented by $0.333 - 0.333\,x$. The dissociation constant of acetic acid has the value 1.8×10^{-5}; by making the proper substitutions in the general equation we get

$$\frac{(0.333\,x)^2}{(0.333-0.333\,x)2}=1.8\times10^{-5},$$

or

$$0.333\,x^2+3.6\times10^{-5}\,x=3.6\times10^{-5},$$

from which we obtain $x = 0.0108$.

Hence the degree of dissociation and the concentration of the ions in any solution of such electrolytes can be calculated if the concentration and dissociation constant are known. It might be

noted that when the total concentration of the electrolyte is 1, and k has a small value the value of x is approximately equal to the square root of k. For instance, the concentration of H+ in a normal solution of acetic acid is

$$1 \times (1.8 \times 10^{-5})^{\frac{1}{2}}, \quad \text{or} \quad 0.00425.$$

Dissociations in Solutions Containing Two Electrolytes Which Yield a Common Ion. It can be shown that when two solutions which contain equal concentrations of the same ion are mixed in any proportions whatever, the dissociation of the two electrolytes in the resulting mixture satisfies the law of mass action if the concentration of the common ion remains unchanged. Such solutions are designated as "isohydric." Solutions of the two electrolytes are isohydric when the product of the concentration of the electrolyte and its degree of dissociation at this concentration is the same for both solutions. When both electrolytes are but slightly dissociated solutions of them are approximately isohydric when their concentrations are inversely proportional to their dissociation constants.

When solutions which are not isohydric are mixed, changes in the dissociation of both electrolytes are inevitable. In such mixtures the concentration of the common ion represents the sum of the concentrations due to the dissociation of both electrolytes. If C represents the total concentration of one electrolyte and C' that of the other, and X and Y their respective degrees of dissociation, the concentration of the common ion is $(CX + C'Y)$, and assuming that they are both weak electrolytes the following expressions are true.

$$(3) \quad k = \frac{CX\,(CX + C_1Y)}{C\,(1 - X)} = \frac{X}{1 - X}(CX + C_1Y).$$

$$(4) \quad k' = \frac{C_1Y\,(CX + C_1Y)}{C_1\,(1 - Y)} = \frac{Y}{1 - Y}(CX + C_1Y).$$

If we divide (3) by (4) we obtain

$$\frac{X}{1 - X} : \frac{Y}{1 - Y} :: k : k',$$

that is, the ratio of the dissociated to the undissociated molecules of one electrolyte bears the same relation to the corresponding ratio for the other, as the dissociation constants of the respective electrolytes bear to each other.

If it is assumed that the second electrolyte is added as a solid, so that the change in volume is eliminated, a reduction in the degree of dissociation of the first electrolyte must take place; this change will be large in proportion as the dissociation constant of the added electrolyte is large as compared with that of the original electrolyte. The degree of dissociation of the added electrolyte must be less than it would have been if added to the same volume of water, and the reduction will be large in proportion as the dissociation constant of the original electrolyte exceeds that of the added electrolyte.

If the second electrolyte is added in the form of a solution the effect of dilution on the dissociation of both electrolytes must also be considered. The action of either electrolyte upon the dissociation of the other is large in proportion as the composition of the two solutions differ from that of isohydric solutions.

The " Repression of Ionization." The most important practical result of the above discussion is to give a better understanding of the phenomenon now known as the "repression of ionization." The chemical activity of certain reagents is greatly diminished by the addition of certain electrolytes which yield a common ion. The addition of potassium acetate to a solution of acetic acid greatly reduces the acidic properties of the latter; the addition of ammonium chloride to a solution of ammonium hydroxide also reduces the basic properties of this reagent. In both cases the reagents added have large dissociation constants, and those originally present have small ones. If the solution of potassium acetate added contains a greater concentration of $C_2H_3O_2$ ion than the acetic acid solution, the degree of ionization of the
er must be reduced, and the concentration of the hydrogen
the resulting mixture must be less than that of the original

solution. Similarly, if the solution of ammonium chloride added is sufficiently concentrated to yield a greater concentration of NH_4 ion than the ammonium hydroxide solution, the degree of ionization of the latter, and hence the concentration of the hydroxyl ion, must be reduced.

Reactions Between Electrolytes Which Do Not Yield a Common Ion. The most important effects to be considered here result from the formation of entirely new compounds. If both electrolytes yield one anion and one cation at least two undissociated molecules, in addition to the two undissociated molecules present in the original solutions, should exist in the resulting mixture. The concentrations of these molecules will depend for the most part upon their respective dissociation constants. If these constants are large their concentrations will be very small, and the resulting mixture will retain for the most part the combined properties of the two constituent solutions. If, however, one of these constants is small this favors the formation of the new molecule at the expense of the ions concerned.

Reactions which Involve the Formation of Water. Pure water dissociates into hydrogen and hydroxyl ions to a very slight extent only; the value of its dissociation constant is 1×10^{-14}. When an acid is added to a base, water and a salt are formed. If both acid and base are strong, and the concentration of the resulting mixture is small, their dissociation may be considered complete, and with but few exceptions the dissociation of the resulting salt can also be considered complete. The essential feature of the reaction therefore is the disappearance of hydrogen and hydroxyl ions and the formation of water; the concentrations of the anion of the acid and the cation of the base remains practically constant. Hence the reaction is expressed by

$$H^+ + HO^- \rightarrow H_2O, \quad \text{and} \quad K = \frac{(H_2O)}{(H^+)\,(HO^-)}.$$

Since $(H_2O) \div (H^+)\ (HO^-)$ is the reciprocal of the expression representing the dissociation constant of water, K has the value

$1 \div 1 \times 10^{-14}$ and therefore all reactions of this type are very nearly complete.

If both acid and base are but partly dissociated the reaction constant may have a small value only. The most important equilibrium concerned in such reactions is expressed by

$$ROH + HA \rightarrow H_2O + R^+ + A^-$$

in which ROH represents a weak base and HA a weak acid. Three other relations must also exist in the final solution, namely:

$$\text{(a)}\ \frac{(R^+)(HO^-)}{(ROH)} = k_b, \quad \text{(b)}\ \frac{(H^+)(A^-)}{(HA)} = k_a, \quad \text{(c)}\ \frac{(H^+)(HO^-)}{H_2O} = k_w.$$

If we multiply (a) by (b) and divide by (c) we obtain the expression

$$\frac{(R^+)(A^-)(H_2O)}{(ROH)(HA)} = \frac{k_a \cdot k_b}{k_w} = K.$$

This expression shows that the value of the constant for this class of reactions depends upon, and can be calculated from, the dissociation constants of the acid and base and of water. If the acid is strong its dissociation constant can be represented with approximate accuracy by one, and the general expression becomes

$$K = \frac{k_b}{k_w}.$$

If the base is strong its dissociation constant can be represented with approximate accuracy by one, and the general expression becomes

$$K = \frac{k_a}{k_w}.$$

Hydrolysis. This represents the converse of the class of reactions just considered. It is expressed by

$$(R^+) + (A^-) + H_2O \rightarrow (ROH) + (HA).$$

The value of K for such reactions is evidently the reciprocal of that representing the formation of a salt and water from a weak acid and a weak base, namely,

$$K = \frac{k_w}{k_a k_b}.$$

Evidently K has a maximum value when k_a and k_b are both very small, but it may be moderately large when either of them has a value which approaches that of k_w.

The effect of hydrolysis is most striking when the salt yields either a strong acid and a very weak base, or a strong base and a very weak acid. In the former case the solution contains a concentration of hydrogen, and in the latter case of hydroxyl ion, which is directly proportional to the extent to which the salt is hydrolyzed, and for this reason solutions of salts representing combinations of strong acids and weak bases show acidic properties and solutions of salts representing combinations of strong bases and weak acids show basic properties. If the dissociation constants of the acid and base formed have the same value the solution will contain equivalent concentrations of hydrogen and hydroxyl ions and hence, such solutions are neutral even though the salt is hydrolyzed to a much greater extent than when one dissociation constant is large and the other small.

Reactions Involving the Displacement of One Acid or Base by Another. When a salt which represents the result of the combination of a base with a weak acid is treated with a second acid a reaction becomes possible which is represented by

$$(R^+)(A^-) + (HA_2) \rightarrow (R^+) + (A_2^-) + (HA)$$

and

$$K = \frac{(A_2^-)(HA)}{(A^-)(HA_2)}.$$

Two other equilibria must exist in the resulting solution, namely,

$$\text{(a)}\ \frac{(H^+)(A_2^-)}{(HA_2)} = k_{HA_2}, \quad \text{and} \quad \text{(b)}\ \frac{(H^+)(A^-)}{(HA)} = k_{HA}.$$

If we divide (a) by (b) and eliminate (H) we obtain

$$\frac{(A_2^-)(HA)}{(A^-)(HA_2)} = \frac{k_{HA_2}}{k_{HA}} = K.$$

Hence the completeness of such reactions increases in proportion as the dissociation constant of the added acid exceeds that of the acid from which the original salt was formed. If the dissociation constant of the added acid can be represented with approximate accuracy by one, the value of K becomes the reciprocal of the dissociation constant of the acid from which the salt was formed.

Similarly it can be shown that the reaction constants of those processes which involve the displacement of one base from a salt by a second base depend upon the ratio of the dissociation constant of the second base to that of the base from which the original salt was formed.

Reactions Involving the Formation of Complex Ions. Certain reactions depend upon the tendency which certain ions possess of combining with other ions or non-ionized molecules to form complex ions. For example, when a soluble silver salt is added to a soluble cyanide a reaction takes place which is represented by

$$Ag^+ + NO_3^- + 2\,K^+ + 2\,CN^- \rightarrow Ag(CN)_2^- + K^+ + NO_3^-.$$

The essential feature of this process is the formation of $AgCN_2^-$ from Ag^+ and $2\,CN^-$, a process which involves the loss of one positive and one negative charge. The mass law requires that

$$\frac{(Ag(CN)_2)^-}{(Ag^+)(CN)^{2-}} = K.$$

K is here a constant which is a numerical expression for the tendency of the complex ion to form and may be designated as the "complex ion constant." In this example it has a very large value, namely, 1×10^{21}, and hence the reaction is practically a complete one.

CHAPTER VII

METHODS OF PRODUCING AND APPLYING HEAT

Sources of Heat Used. Many quantitative operations depend for their success upon the maintenance of definite temperatures for either long or short time intervals. The range of temperatures used is wide, and a great number of devices become desirable or necessary if efficiency and speed are to be attained. Altho it costs less under normal conditions to produce heat by the consumption of gas than of electrical energy, the latter method is more directly and easily controlled, and frequently the difference in cost is more than offset by the greater certainty with which it can be used, and the absence of undesirable products of combustion.

Heating with an Electric Current. The amount of heat produced by the passage of a current through a resistor varies with the product of the resistance offered and the square of the current transmitted, and, therefore, depends upon the current strength to a greater extent than the resistance. Various materials are used as resistors in constructing devices for this purpose; the most convenient are certain alloys, such as German silver, monel metal, and nichrome, which possess a high specific resistance, a high melting point and ability to resist oxidation at high temperatures. The alloy last named possesses all of these properties to a maximum degree and can be obtained at small cost in wire or ribbon of any desired size.

In constructing an electric heating device the factors of greatest importance are the voltage of the current available, which may be either direct or alternating, the masses and specific heats of the substances used in its construction, the losses from radiation, and

the temperature which it is desired to attain. If the voltage is fixed the length and size of the wire used as a resistor are the essential features to be decided on, and, owing to the large number of variables concerned, this must be determined by experiment rather than by calculation. It may be noted, however, that a long piece of coarse wire forms a more durable resistor than a short piece of fine wire which has an equal resistance. The temperature attained with such devices is fairly constant so long as the voltage and radiation losses are constant. It can be reduced by reducing the voltage, and is therefore easily regulated, that is for temperatures attained with the maximum voltage, by introducing a rheostat in the circuit.

Devices Used for Evaporation. The evaporation of solutions rarely necessitates the use of temperatures greatly in excess of 100°. Temperatures somewhat below this point, but sufficient for the evaporation of most aqueous solutions, are conveniently attained by the use of a "steam bath," that is, a vessel in which water is made to boil vigorously, either by a coil of steam pipes or by the flame of a gas burner, and which has a cover provided with openings for the receptions of the vessels containing the solutions to be evaporated. A bath of a sufficient size to accommodate a large number of such vessels is an essential part of the equipment of a quantitative laboratory. It has the great advantage of keeping the solutions at a uniform temperature well below the point at which mechanical losses are to be anticipated.

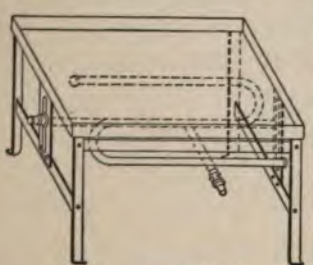

Fig. 7.—Sand Bath

Direct heating of the vessel containing the solution by a flame is usually avoided by interposing a plate of metal, forming a "hot-plate," or a tray filled with sand, forming a "sand bath," between the flame and the vessel. A sand bath of this character is represented in Fig. 7. It gives a higher temperature,

and, therefore, more rapid evaporation than the steam bath, and can be controlled by varying the gas supplied to the burner or the thickness of the layer of sand used. It is especially useful where the liquid is retained in a flask and gentle ebullition is not objectionable.

When it becomes necessary to attain still higher temperatures, as in the evaporation of sulfuric acid, the vessel containing the substance to be evaporated may be placed inside a "muffle," that is, an outer shell which protects the inner vessel from the flame and permits it to be heated by radiation only. A large nickel or iron crucible can be used as a muffle for this purpose, but the device represented in Fig. 8, which is made of heavy asbestos board and bound with sheet iron, is more durable.

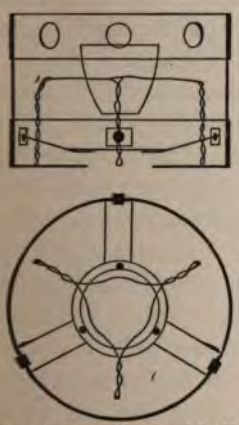

Fig. 8. — Asbestos Muffle

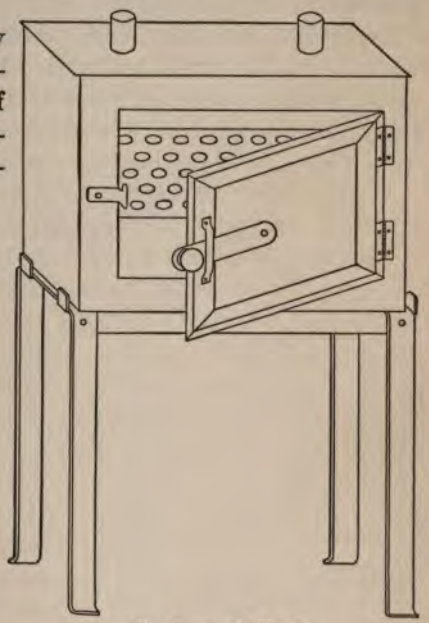

Fig. 9. — Air Bath

Devices for Drying Solids. The amount of vapor to be expelled in drying solids is usually small, as compared with that expelled in evaporating liquids, and the apparatus used may take the form of a rectangular oven, such as is represented in Fig. 9.

Its temperature can be roughly regulated by varying the height of the flame or the size of the burner by which it is heated; if greater refinement is necessary an automatic gas-regulator, which increases or decreases the gas supply as the temperature falls below or exceeds that for which the regulator is set, can be used. Ovens of larger size which are used for cooking and can be obtained from hardware dealers can often be used to advantage.

Still another device, represented in Fig. 10, consists of a double-walled oven, in which the intervening space is filled with a liquid whose boiling point is slightly above the temperature desired. This liquid is kept at the boiling point by means of a burner, and the vaporized liquid is condensed and returned to the oven as fast as produced. The liquids most frequently used are water, which gives a temperature of about 96°, and toluene which gives a temperature of nearly 105°. In all devices of the oven type the water vapor which is generated escapes but slowly and their efficiency, that is, the rate at which drying is affected, is not great.

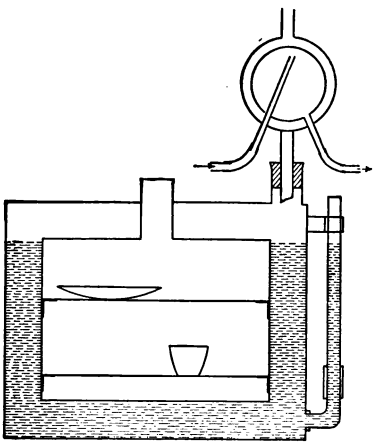

Fig. 10.—Constant-temperature Oven

A further objection to ovens heated by gas is that some of the combustion products may enter the oven and produce objectionable effects upon the substance being dried. For this reason the electrically heated ovens, which can now be purchased from dealers in chemical apparatus, are to be preferred to all others; their cost, however, is somewhat large.

Temperatures Attainable by the Use of Gas Burners. Direct heating of the substance in a crucible is always to be preferred where there is no danger of exceeding the maximum permissible

temperature. The temperature actually attained inside of the crucible depends upon the type of burner used, the calorific value of the gas burned, and the masses and specific heats of the substances heated, that is, the crucible used, the triangle used to support it, and the substance which it contains.

The Bunsen burner is decidedly inferior to the more recently devised Méker burner, a vertical projection of which is represented in Fig. 11. In the former the air supplied at the base is not sufficient for the gas burned and a long cone-shaped flame results; the area over which active combustion takes place is comparatively large, and the highest temperature is attained at the apex of the inner blue cone. In the Méker burner the air supplied at the base is sufficient, but "striking back" is prevented by the grid and enlargement at the outlet; the entire combustion takes place within a few millimeters of the top of the grid, and the heating effect is therefore concentrated in a single horizontal plane.

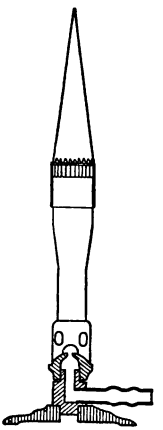

Fig. 11.—Méker Burner

The temperatures actually attained in the interior of uncovered crucibles of different sizes and materials, which were heated on triangles of nichrome wire by the two forms of burners, are given in the following table:

Crucible heated	Berlin porcelain 00	Berlin porcelain 0	Berlin porcelain 1	Platinum	
Capacity	10 cc.	15 cc.	23 cc.	14 cc.	29 cc.
Temperature with Bunsen burner	820°	780°	720°	840°	780°
Temperature with Méker burner	880°	840°	770°	890°	805°

Somewhat higher temperatures are attained by using covers on the crucibles, but this prevents the circulation of air within the crucible and the escape of gases which may be liberated by the substance heated in the crucible, both of which effects are undesirable.

Still higher and more uniform temperatures can be reached by surrounding the burner and crucible with a shield, which cuts off air-currents and greatly reduces the radiation losses. This device is utilized in the burner devised by Chaddock, a vertical projection of which is represented in Fig. 12. Combustion of the gas used is effected exactly as in the Bunsen burner, but the entire burner is made of porcelain, and a fire-clay chimney which fits upon it loosely both reduces the losses from radiation and forms a support for a triangle over which a crucible can be heated.

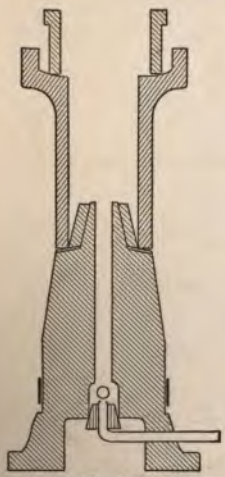

Fig. 12. — Chaddock Burner

Where still higher temperatures are needed a "blast lamp," that is, a burner which is supplied with a blast of air, or an electric furnace can be used. An effective blast lamp is capable of producing a temperature of 1100° in a platinum crucible of moderate size.

Construction of an Electric Furnace. Small electric furnaces designed to heat crucibles of moderate size, which can be purchased from dealers, are extremely advantageous. The plan of an inexpensive and easily constructed furnace is represented in vertical and horizontal projection in Fig. 13. The heating unit consists of an alundum core (A) two inches in diameter, around which is wound 15 feet of No. 23 nichrome wire coiled in the form of six four feet long and one-eighth of an inch in diameter.

The core and helix rest upon a piece of asbestos board supported by a ring of porcelain (B); it is placed in the center of a cylinder of sheet copper some four inches in diameter, which is supported in a vertical position by means of a wooden base (C); but is insulated from the base by strips of thick asbestos. The entire space between the core and cylinder is filled with a compact mass of asbestos. The ends of the helix are brought thru but insulated from the copper cylinder and attached to binding posts screwed into the base.

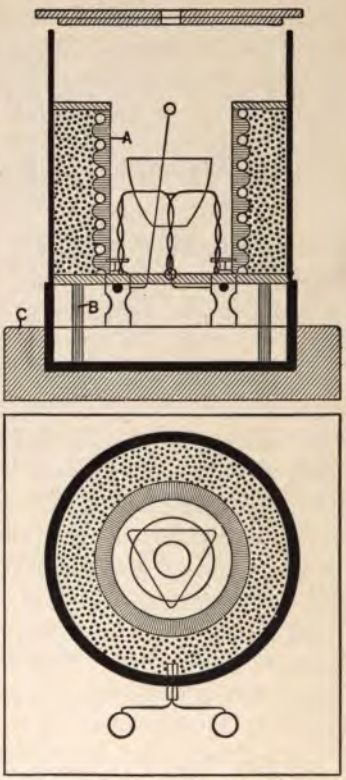

Fig. 13.— Plan of an Electric Furnace

When this furnace is attached to a 110-volt circuit it consumes about 3 amperes of current. When a crucible is placed inside the core and the furnace is covered, the temperature inside the crucible rapidly rises to 1000°. A lower temperature can be attained by placing a rheostat in series with it, but it is more economical to construct other furnaces which offer a greater resistance where lower temperatures are desired.

CHAPTER VIII

THE REMOVAL OF UNDESIRABLE CONSTITUENTS BY EVAPORATION

Factors to be Considered. It is frequently necessary to reduce the volume of the solution containing the substance being analyzed or to eliminate certain volatile constituents by evaporation. The factors which determine the rate at which evaporation takes place are the vapor pressure of the solution at different temperatures, the rate at which the vapor formed is carried away from the surface of the liquid, the extent of this surface and, where the temperature used is that of the boiling point, upon the efficiency of the heating device employed. The phenomenon of boiling is due to the fact that bubbles of vaporized liquid are constantly forming at the bottom or in the interior of the mass of liquid and passing to its surface; these bubbles are often projected above the surface of the liquid with considerable violence, and may carry with them small quantities of the solution being evaporated. Hence, unless a special form of apparatus is used, which prevents the escape of these particles, appreciable losses of the non-volatile constituents of the solution may occur. This difficulty is somewhat intensified by the phenomenon of "superheating," in which portions of the liquid which are in immediate contact with the bottom of the containing vessel are temporarily heated above the normal boiling point and then suddenly vaporized, it can be avoided by agitating the liquid, or by adding to it a small piece of platinum wire or some other good conductor of heat.

If a mixture of a solid and a liquid is being evaporated the phenomenon known as "bumping" may occur. It is due to the

fact that the solid, especially when it has a high specific gravity, packs together on the bottom of the containing vessel, and bubbles of vapor accumulate between this layer and the bottom of the vessel. Their pressure finally overcomes that of the layer and in escaping they throw masses of the mixture out of the vessel with considerable violence. This difficulty does not arise if the temperature is kept somewhat below the boiling point, or if the mixture is stirred vigorously.

Evaporation can be greatly hastened by sucking the vapor formed from the containing vessel by means of a suction pump, or by directing a current of air against the surface of the liquid by means of a force pump. Either device cools the surface appreciably, but as a more efficient heating device can then be used, the rate of evaporation can be greatly increased.

Methods of Effecting Evaporation. Two extremes are represented in the methods used to effect rapid evaporations. Either the liquid is placed in a shallow evaporating dish and heated to a temperature somewhat below its boiling point, or it is placed in a flask or narrow beaker and boiled violently. The latter method is somewhat more rapid but requires care and watchfulness on the part of the analyst, and is always subject to the possibility of small mechanical losses. Where the former method is used, a heating device which permits of a rapid and constant control of the temperature is necessary. Direct heating over a flame, even though the vessel is protected from it by a piece of wire gauze, is not to be recommended. The use of a water or "steam bath," which insures a temperature somewhat below 100°, is usually very satisfactory. A sand bath, or a hot plate give higher temperatures and more rapid evaporation but involve possibilities of mechanical losses.

Evaporation of Mixtures of Two Volatile Substances. When two substances, which possess appreciable vapor pressures and form homogeneous solutions, are mixed together a reduction in the vapor pressures of both constituents takes place, and the sum

of the vapor pressures of the two constituents in the mixed vapor phase is less than the sum of the vapor pressures of the pure substances at the same temperature. The extent to which one constituent of such a mixture lowers the vapor pressure of the other, varies with different pairs of liquids, but all known examples belong to one of three types. These types can be differentiated most readily by plotting the curves representing the total vapor pressures of the two constituents in the mixed phase corresponding to all possible mixtures of these constituents. Such curves are represented in Fig. 14, in which the ordinates represent vapor pressures,

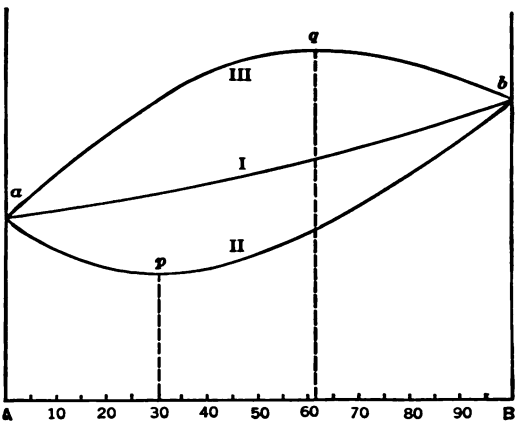

Fig. 14. — Curves Representing Vapor Pressures of Mixed Liquids

and the abscissas the comparative amounts of the two constituents *A* and *B*. In type I the total vapor pressure of the mixture increases continuously from *a*, corresponding to the pure constituent *A*, to *b*, corresponding to the pure constituent *B*. In type II the total vapor pressure attains a minimum value at *p*, that is, it is reduced by adding *B* to pure *A* or *A* to pure *B* up to the concentration which yields the minimum value *p*. In type III the total pressure attains a maximum value at *q*, that is, it is increased by adding *B* to pure *A* or *A* to pure *B* up to the concentration which

gives the maximum value q. Since the boiling points of such mixtures depend directly upon the sum of vapor pressures of the two constituents the boiling points of mixtures representing type I decrease continuously as the percentage of that constituent which has the greater vapor pressure increases; whereas the boiling points of mixtures representing type II attain a maximum and those of type III attain a minimum at certain concentrations of the two constituents. If then mixtures belonging to type II are continuously evaporated the composition of the mixture changes up to the point at which it has the maximum boiling point; those representing type III must change up to the point at which it has the minimum boiling point. Mixtures which are characterized by constant boiling points yield mixed vapor phases in which the relative amounts of the two constituents are the same as in the corresponding liquid phases.

Removal of Acids by Evaporation. The mixtures of this kind which are most frequently dealt with in quantitative work are aqueous solutions of acetic, hydrochloric, nitric and sulfuric acids; the first three of these mixtures belong to type II. The rate at which any one of these acids is driven out of an aqueous solution thru evaporation depends mainly upon the concentration of that acid in the mixed vapor phase. Useful data can therefore be secured by evaporating aqueous solutions of these acids at their boiling points, condensing and collecting the vapor given off at definite time intervals, and determining the composition of the condensed liquid and of the solutions from which they were distilled. The results of a series of determinations * of this kind are given in the curves of Fig. 15. The ordinates represent the percentages of the various acids in the distillates and the abscissas those of the acids in the corresponding solutions.

These curves at once show the comparative volatilities of the different acids and the concentrations which must be attained before they can be driven out with even reasonable rapidity by

* From experimental data obtained by the writer.

evaporation. It will be noted that in evaporating solutions of acetic acid the concentration of the liquid increases at a uniform rate until the residual solution contains about 80 per cent. Solu-

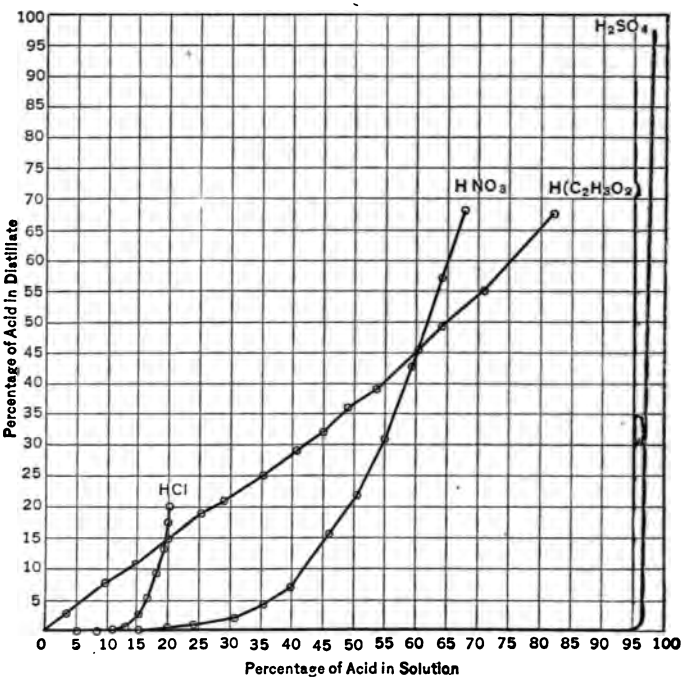

Fig. 15. — Curves Showing the Changes in Concentration which Result when Dilute Acids are Distilled

tions of hydrochloric acid concentrate very rapidly at first, then more slowly until a mixture which has a constant maximum boiling point of 110°, and contains 20.2 per cent of acid, is obtained. The behavior of nitric acid resembles that of hydrochloric, but the constant-boiling mixture contains 68 per cent of acid, and boils at 120°. Sulfuric acid on the other hand is not appreciably volatilized until the solution has attained a concentration of about 98

per cent, which requires a temperature of more than 250°. Complete removal of any of these acids cannot be effected unless the solution is evaporated to dryness; the total amount left in any solution which has been concentrated to a constant boiling point mixture can be calculated from the volume left and the composition of this mixture.

The theory of the removal of acids from solutions containing two or more acids is not so easily followed, for, altho the addition of a second acid reduces the volatility of the first, interaction between the two acids may take place. Thus when both hydrochloric and nitric acids are present a reaction represented by the equation given below becomes possible:

$$HNO_3 + 3\,HCl \rightarrow NOCl + 2\,H_2O + Cl_2.$$

The reaction constant has a relatively small value, and unless the concentrations of the two acids are large but little chlorine is liberated. At high concentrations and especially at moderately high temperatures the NOCl formed breaks down into NO and Cl_2, and complete decomposition and expulsion of the acid which is not present in excess is rapidly effected. Hence it is possible to expel either acid by adding an excess of the other acid, and evaporating the solution sufficiently.

CHAPTER IX

THE CALCULATION OF RESULTS

Calculation of Chemical Factors. The general formula for the calculation of the results of any direct gravimetric process is

$$\frac{\text{Weight of substance separated}}{\text{Weight of sample used}} \times f \times 100 = \text{desired percentage.}$$

In this formula f represents the factor by which the weight of the separated substance must be multiplied to give the equivalent weight of the substance whose percentage is to be reported. Since the substance weighed and the substance reported may have the same chemical formula, f may have the value 1; usually it has a different value, which may be either greater or less than 1, and can be calculated from the atomic and molecular weights of the substances concerned. If a precipitate of $Mg_2P_2O_7$ has been separated, and it is desired to report the percentage of P present, it would be reasoned that every molecule of $Mg_2P_2O_7$ separated represents two atoms of P in the sample, and hence the desired factor is obtained by dividing two times the atomic weight of phosphorus by the molecular weight of magnesium pyrophosphate. If a precipitate of Fe_2O_3 has been separated, and it is desired to report the Fe_3O_4 present, the reasoning would be that for every three molecules of Fe_2O_3 found, two of Fe_3O_4 must have been present and the proper factor to employ is $2\ Fe_3O_4 \div 3\ Fe_2O_3$. It should be especially noted that the number and character of the reactions concerned in the production of the substance which is separated from the sample are of no significance. When a substance which contains Fe_3O_4 is analyzed by separating Fe_2O_3

from it, it can be assumed that since the process is a quantitative one all of the iron present as Fe_3O_4 is transformed into Fe_2O_3, and, further, that no additional iron in any form is introduced.

Determination of Chemical Factors Experimentally. The value of f can also be determined experimentally by submitting a sample containing a known percentage of the substance which is to be reported upon to the process concerned, and calculating the ratio of the weight of the substance known to be present in the sample used to the weight of product separated. An empirically determined factor of this kind is subject to errors of the same kind and magnitude as those concerned in the actual determination. If the process is a complex one, in which subsidiary reactions are possible, and large errors of any kind are to be expected, the empirically determined factor is the logical one to use, for by using it the errors involved in the actual determination are partly or wholly counterbalanced. If the process is based upon a few simple and definite reactions and is not subject to any large errors the calculated factor should be used, since it is based upon experimental work of much greater accuracy than that employed in the determination of the empirical factor.

The System of Atomic Weights Used. The atomic weights of the various elements are calculated with respect to the atomic weight of hydrogen with a value of 1, or with respect to that of oxygen with a value of 16. The actual ratio of the atomic weights of these elements is 1.008 : 16 and, hence, the systems based upon the two standards differ slightly. In calculating the factors used in analytical chemistry either system may be used with equal accuracy, provided all the weights made use of are referred to the same system, and with about equal facility. The atomic weights which will be used in this book are those adopted by the International Committee on Atomic Weights in 1916.

Form in Which Results Are Reported. The form in which the results of an analysis is reported admits of some degree of choice, which depends largely upon the object for which the analysis is

Element	Symbol	Atomic weight	Element	Symbol	Atomic weight
Aluminum	Al	27.10	Mercury	Hg	200.6
Antimony	Sb	120.20	Molybdenum	Mo	96.00
Arsenic	As	74.96	Nickel	No	58.68
Barium	Ba	137.37	Nitrogen	N	14.01
Bismuth	Bi	208.00	Oxygen	O	16.00
Boron	B	11.00	Phosphorus	P	31.04
Bromine	Br	79.92	Platinum	Pt	195.20
Cadmium	Cd	112.40	Potassium	K	39.10
Calcium	Ca	40.07	Selenium	Se	79.20
Carbon	C	12.00	Silicon	Si	28.30
Chlorine	Cl	35.46	Silver	Ag	107.88
Chromium	Cr	52.00	Sodium	Na	23.00
Cobalt	Co	58.97	Strontium	Sr	87.63
Copper	Cu	63.57	Sulfur	S	32.06
Fluorine	F	19.00	Tellurium	Te	127.50
Gold	Au	197.20	Thallium	Tl	204.00
Hydrogen	H	1.008	Tin	Sn	118.70
Iodine	I	126.92	Titanium	Ti	48.10
Iron	Fe	55 84	Tungsten	W	184.00
Lead	Pb	207.20	Uranium	U	238.20
Lithium	Li	6.94	Vanadium	V	51.00
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	90.60

made. In general, it is advisable to report all results in such a form as will indicate most nearly the actual composition of the sample. Thus, if nitrogen is determined and reported as such, there is no means of knowing which one of the various forms in which that element may be combined is represented, whereas if the report is in terms of NH_3, N_2O_5 or N_2O_3, the presence of corresponding percentages of ammonia, of nitrates or of nitrites is clearly shown. Since oxygen, unless it is in the free condition, is but rarely determined it is customary to combine it with the metals or metalloids actually present in the report made. This makes it readily possible to show the degree of oxidation of these elements and to account for everything present, that is, to make the analysis sum up to 100 per cent. Thus in the analysis of

crystallized ferrous sulfate it is desirable to report the percentages of FeO, SO_3 and H_2O rather than Fe, S, and H.

It should be noted that if salts, such as chlorides or sulfides, which do not contain oxygen, are present, and all of the bases present are reported as oxides, more oxygen will be included in the summation than is actually present. The proper correction is then made by subtracting the oxygen equivalent of the chlorine and sulfur from the summation; this then appears in the summary as "less oxygen due to chlorine and sulfur."

When a solution is submitted to analysis it is now customary to report the ions present. Formerly an attempt was made to calculate and report the probable salts present, that is, to combine the acidic and basic radicals according to certain arbitrary rules. This method is misleading if the validity of the electrolytic dissociation theory is granted.

Abbreviation of Calculations. Altho the calculations of analytical chemistry involve simple multiplications and divisions only it will be found advantageous to make use of logarithms or of a slide rule. Where a large number of determinations are made by the same process and the same chemical factor is used, time can be saved by preparing a table showing the values of those multiples of this factor which may be needed most frequently. Still another method of arriving at the same result is to plot a curve, in this case a straight line, showing the relation between this factor and certain multiples of it. Many handbooks containing tables of this kind and other information frequently needed by the analytical chemist have been prepared.*

Another device which is sometimes used is to employ "factor weights" in making the analysis. If the quantity of sample employed is made equal to f of the general formula the desired percentage is exactly 100 times the weight of the separated sub-

* Van Nostrand's Chemical Annual by J. C. Olsen; Chemists' Pocket Manual by R. Meade; Laboratory Calculations and Specific Gravity Tables by Adriance; Conversion Tables for Iron Analysis, by Allen.

stance. If the factor weight is larger or smaller than it is desirable to use, a simple fraction or multiple of it can be used with nearly equal advantage.

Calculation of Indirect Determinations. It is sometimes advantageous to analyze certain kinds of mixtures by so-called "indirect methods." Thus it is possible to calculate the percentages of sodium and potassium chlorides in mixtures of these salts from the total percentage of chlorine in the mixture, which can be easily determined with great accuracy. If the percentage of sodium chloride in such a mixture be represented by x, then $100 - x$ must represent the percentage of potassium chloride, and if the percentage of chlorine in it be represented by a, the following relation is true:

$$x\frac{\text{Cl}}{\text{NaCl}} + (100 - x)\frac{\text{Cl}}{\text{KCl}} = a,$$

from which the percentages of sodium and potassium chlorides are easily calculated.

Another method of attaining the same result consists in ascertaining the factor representing the relation between a known weight of the mixture and the weight obtained when the chlorides present are completely changed into sulfates, which change is easily effected by evaporating with an excess of sulfuric acid. If this factor be represented by b, the following relation is true:

$$x\frac{\text{Na}_2\text{SO}_4}{2\,\text{NaCl}} + (100 - x)\frac{\text{K}_2\text{SO}_4}{2\,\text{KCl}} = 100\,b,$$

from which the desired percentages can be calculated.

The former process is based upon the difference between the ratio Cl ÷ NaCl and the ratio Cl ÷ KCl. This amounts to only 0.131 and an error in the determination of chlorine in the unknown mixture is multiplied by 1 ÷ 0.131 or 7.64 in the percentages reported. This suggests the chief objection to such processes, that is, relatively small errors in the determination of chlorine in the mixture and the presence of small amounts of

additional substances make large errors in the final results. The second process depends upon the difference between the ratio $K_2SO_4 \div 2\,KCl$ and $Na_2SO_4 \div 2\,NaCl$, which has the value 0.0465 and considered from this standpoint is less desirable than the first process.

Calculation of Chemical Formulæ. The analytical chemist is sometimes required to calculate the probable formula of an unknown substance from the results of his analysis. If each of the percentages obtained are divided by the respective atomic or molecular weights, a series of figures are obtained which represent the relative number of atoms or molecules present in the molecule whose formula is sought. The numbers actually obtained will not usually be entire integers and some of them may be less than unity. Since no chemical formula which involves the use of fractions is permissible it becomes necessary to multiply or divide the entire series by a factor which will most nearly reduce them all to whole numbers. The simplest method of procedure is to first note which of the series has the smallest value, and to divide the entire series by this value. The results represent the simplest formula which can be assigned to the substance; the correct formula cannot be calculated unless the molecular weight is also known.

For example the analysis of an unknown mineral gave the series of figures which appear in the first column given below:

K_2O = 15.41 ÷ 94.3	= 0.1634	1.00
MgO = 6.58 ÷ 40.36	= 0.1630	1.00
CaO = 18.80 ÷ 56.10	= 0.3351 ÷ 0.163 =	2.05
SO_3 = 52.91 ÷ 80.07	= 0.6597	4.05
H_2O = 5.84 ÷ 18.02	= 0.3241	1.99

Dividing by the proper molecular weights gives the figures which appear in the third column, and dividing these by 0.163 those of the last column. The simplest probable formula of the mineral is therefore $K_2MgCa_2(SO_4)_4 \cdot 2\,H_2O$, which represents the mineral polyhalite.

Calculation of Volumes of Gases. The analytical chem frequently finds it necessary to calculate the volumes occup by specified weights of solids or liquids after they have b changed into the gaseous state. Such calculations are ea carried out by making use of the fact that one mole of any gase substance when measured at zero degrees and 760 mm. pressu occupies a volume of 22.4 liters. Another form of this relat is expressed by the statement that the weight of one liter oxygen under these conditions is 1.428 gm. and that of any equals 1.428 times the ratio between the molecular weight of t gas and the molecular weight of oxygen.

Changes in volume resulting from changes in pressure easily calculated by use of the Law of Boyle, the variations fr which are small if the gas concerned is well above its crit temperature, and the pressure does not exceed an atmosph According to this law, if v represents the volume of a gas at p sure p, its volume v' at the pressure p' is found by the relatio

$$v' = v\frac{p}{p'}.$$

Changes in volume resulting from changes in temperature usually calculated with sufficient accuracy from the Law of G Lussac. According to this law if v represents the volume o gas at the temperature t its volume v' at the temperature t calculated from the relation

$$v' = \frac{273 + t'}{273 + t}.$$

SECTION II

GAS-EVOLUTION PROCESSES

CHAPTER X

GENERAL FEATURES OF GAS-EVOLUTION PROCESSES

The Decomposition of Carbonates. The simplest examples of this class of determinations are those in which the formation of a gaseous product is effected by a change in temperature. The determination of carbon dioxide in certain carbonates furnishes a good illustration. The decomposition of calcium carbonate is expressed by the reaction

$$CaCO_3 \rightarrow CaO + CO_2.$$

The system here represented consists of two solid phases, each of which is a pure substance and therefore has a constant concentration, and a gas phase, the composition of which can vary. Since the concentrations of $CaCO_3$ and CaO in the solid phases are constant the concentrations of these substances in the gas phase must remain constant so long as appreciable amounts of the two solids are present and can be represented by k and k' respectively. The expression for the equilibrium in the gas phase then becomes

$$K = \frac{k'\,(CO_2)}{k},$$

which can be reduced to $K\frac{k}{k'} = (CO_2)$, or $K' = (CO_2)$.

That is, a constant which is a simple multiple of the true equilibrium constant and which, unlike the latter, can be determined

experimentally, may be used in place of the true equilibrium constant in discussing chemical equilibria in this and all similar reactions.

Since equal volumes of all gases, when measured at the same temperature and pressure, contain the same number of molecules (Avogadro's hypothesis), the pressures exerted by all gases are proportional to their concentrations and can be used as a measure of the latter. The total pressure exercised by the gas phase in contact with a mixture of CaO and $CaCO_3$ must equal that of the atmosphere, unless contained in a closed vessel, and since the pressures exerted by each of these gases are independent of each other (Dalton's Law) each kind of gas can be thought of as exercising a "partial pressure," and if so the sum of the partial pressures of all the gases represented must equal that of the atmosphere.

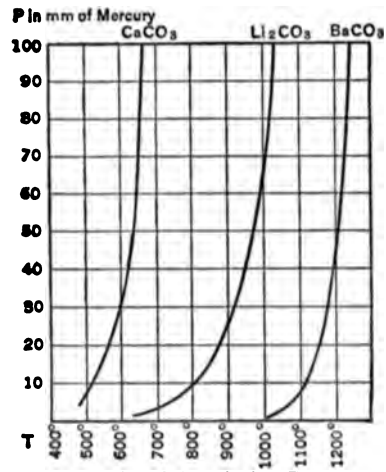

Fig. 16. — The Dissociation Pressures of Carbonates

Hence the value of K' in the preceding expression can be expressed in terms of the number of mm. of mercury to which the partial pressure of the carbon dioxide in equilibrium with CaO and $CaCO_3$ is equal. If such a mixture is in contact with a gas phase in which the partial pressure of the carbon dioxide is less than K' more carbonate will decompose, and the partial pressure of the carbon dioxide will increase; if the partial pressure is greater than K' carbonate will be formed and the partial pressure of the carbon dioxide will decrease.

The effect of varying temperature upon the dissociation pressures of the carbonates of calcium, lithium and barium is shown

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which can be reduced to $K\frac{k}{k'} = (CO_2)$, or $K' = (CO_2)$.

That is, a constant which is a simple multiple of the true equilibrium constant and which, unlike the latter, can be determined

in which P represents the partial pressure of the water vapor present in the vapor phase which is in equilibrium with the two solids. If the condition of equilibrium has not been reached the direction in which the reaction will progress depends upon the relative values of K and the partial pressure of the water vapor in contact with the salt.

Many salts are able to form a series of hydrates each of which contains a definite number of molecules of water, and are not stable unless the concentration of the water vapor by which they are surrounded lies between certain limits, which vary with the temperature. The complete dehydration of such salts is represented by a series of reactions.

The Dehydration of Crystallized Copper Sulfate. This salt, which contains five molecules of water, is stable under ordinary atmospheric conditions, because the partial pressure of the water vapor normally present in the atmosphere exceeds the dissociation pressure of this hydrate at 20°. By increasing the temperature or reducing the concentration of the water vapor surrounding the salt a series of reactions resulting in the formation of $CuSO_4 \cdot 3\,H_2O$, $CuSO_4 \cdot H_2O$ and $CuSO_4$ can be made to take place. The conditions necessary to effect these different transformations are indicated by the series of curves shown in Fig. 17, in which the ordinates represent water-vapor pressures and the abscissas temperatures. The curve CO indicates the series of temperatures and pressures at which the penta- and trihydrate are in equilibrium; DO those at which the tri- and

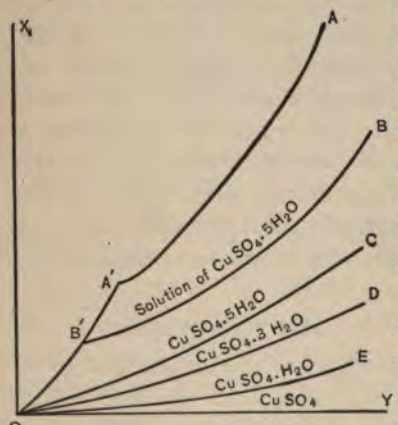

Fig. 17.—Vapor Tensions of Hydrates of Copper Sulfate

monohydrates are in equilibrium; and *EO* those at which the monohydrate and the anhydrous salt are in equilibrium. The space between *CO* and *DO* represents the only series of conditions at which the trihydrate is stable, that betweer *DO* and *EO* the only conditions under which the monohydrate is stable, and that below *EO* the only conditions under which the anhydrous salt is stable. Complete dehydration can be effected within the range of conditions represented by the field *EOY*.

The Evolution Method. The weight of the gas liberated by such reactions as those under discussion can often be estimated by determining the total loss in weight of the apparatus in which the reaction takes place, that is, by determining the weight of liberated gas by the "evolution method." In general, there are two extremes represented in the method of procedure adopted. In one the temperature is kept very high, and no attempt made to reduce the partial pressure of the liberated gas below that normally present; in the other the temperature is kept low, and the partial pressure of the liberated gas is artificially reduced. Where, owing to volatilization of the residual product or to other changes which affect its weight, the maximum temperature which can be used is too low to cause complete and rapid decomposition of the sample, it is desirable or even necessary to reduce the partial pressure of the liberated gas by passing a current of air, or some other gas, over the sample. This necessitates the use of a somewhat elaborate apparatus similar to that used for the direct method described in the next paragraph.

The Absorption Method. Since the residual compound is often hygroscopic, and, therefore, difficult to weigh, and since it is sometimes impossible to entirely avoid reactions involving changes in weight in addition to the one desired, it is sometimes necessary to pass the liberated gas into an apparatus which absorbs it completely, and determine its weight by the direct or "absorption method." The decomposition must then be made in a closed vessel and all of the liberated gas washed thru the absorb-

ing apparatus by means of a current of air, or some other gas which contains no substances which are also taken up by the absorbing apparatus.

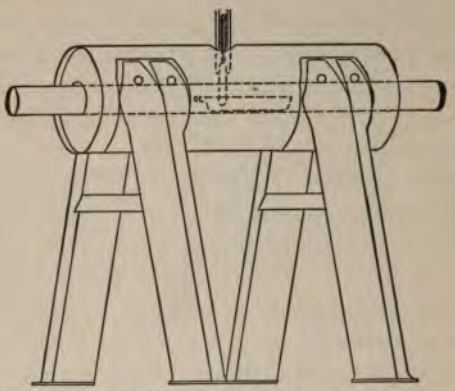

Fig. 18. — Muffle Furnace for Heating Tubes

When the liberated gas is to be determined by the absorption method, or when a gas is to be passed over the substance to be analyzed and determined by the evolution method, an apparatus similar to the one represented in Fig. 18 becomes necessary. This consists of a cylindrical muffle of sheet nickel or monel metal supported horizontally on four legs and enclosing a glass tube, the diameter of which is sufficiently large to contain a porcelain "boat," which holds the substance to be analyzed. The temperature of the air space within the muffle, which is somewhat higher than that of the substance within the boat, can be measured with a thermometer. It is possible to heat the substance in such an apparatus by means of a single Bunsen burner up to as high as 350° and where the danger of exceeding the maximum permissible temperature is but small, an opening can be made in the bottom of the muffle and

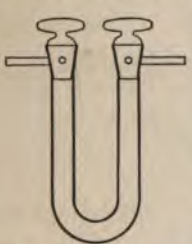

Fig. 19. — Glass-stoppered U-tube

the tube heated directly, even up to the point at which the glass begins to soften. Where still higher temperatures are necessary, a tube of porcelain should be used.

The absorption of the liberated gas can be effected in several types of apparatus, which should be as light and compact as possible. For solid absorbents a U tube, as represented in Fig. 19, is most convenient; for liquid absorbents a U-tube containing pieces of pumice stone saturated with the liquid, or certain special forms of absorption bulbs such as that of Geissler, Fig. 20, can be used.

General Theory When the Reagent Is a Gas. Reactions resulting in the liberation of a gas, which are brought about by the addition of a reagent, form the basis of many useful quantitative processes. The reagent itself may be a gas, in which case the system concerned is one involving equilibrium between one or more solid phases and a mixed gas phase. The method of "combustion" invariably used for the determination of carbon and hydrogen in organic compounds is representative of this class. They involve reactions similar to

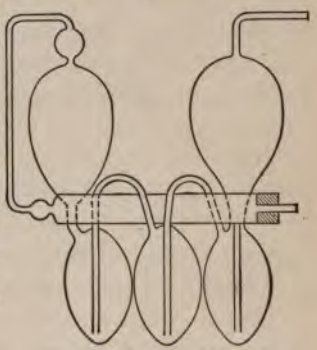

Fig. 20. — Geissler Bulb

$$C_{12}H_{22}O_{11} + 12\,O_2 \rightarrow 12\,CO_2 + 11\,H_2O.$$

Altho this reaction is not appreciably reversible the tendency for formation of intermediate oxidation products, such as carbon monoxide, is reduced to a minimum and the speed of the reaction is increased by keeping the concentration of the oxygen large and that of the carbon dioxide and water vapor small. In general, in all processes dependent upon reactions of this type it is desirable to keep the concentrations of the gases formed low and that of the gaseous reagent used high. This is easily effected by use of the apparatus already described, that is,

by placing the substance to be analyzed in a narrow tube, and passing the gas used as a reagent over it.

General Theory When the Reagent Is a Liquid. When the reagent used is a liquid, the system concerned involves equilibrium between a liquid, a gas and a solid, as, for example, in the reaction:

$$CaCO_3 + 2\,H^+ + 2\,Cl^- \rightarrow Ca^{++} + 2\,Cl^- + H_2O + CO_2.$$

If we disregard the concentration of water, which in the solutions usually used remains practically constant, the expression for equilibrium reduces itself to

$$K = \frac{(Ca^{++}) \cdot (CO_2)}{(H^+)^2}.$$

Evidently such reactions can be made complete if the concentration of the reagent used can be made sufficiently large, and the solubility of the liberated gas can be made sufficiently small.

The weight of the liberated gas can be determined by the evolution method, the absorption method, or by direct measurement of its volume, and calculation of the corresponding weight. For the evolution method a large number of special forms of apparatus, which are known as alkalimeters, can be employed. One of these is represented in Fig. 23, in which *A* represents the receptacle which contains the substance to be analyzed, and in which the reaction takes place, *B* the receptacle for the reagent used, and *C* the receptacle for the reagent used to dry and purify the liberated gas. The weight of the entire apparatus as first charged with sample and reagents, and again after the reaction has been completed, is accurately determined; the difference gives the desired weight of the liberated gas.

For the absorption method an apparatus similar to the one represented in Fig. 24 is used. The essential features are again a container for the reagent, a container for the substance to be analyzed, which also serves as the vessel in which the reaction takes place, one or more absorbing tubes by which the liberated

gas is dried and purified, and an absorption apparatus containing the proper reagents for the retention of the gas which is to be weighed.

General Theory When the Reagent Is a Solid. The salts of certain acids, especially H_2CO_3, HCl, HNO_3 and $HClO_3$, are completely decomposed with the liberation of a gas by heating them with certain oxides such as SiO_2 or B_2O_3, or with certain acid salts such as $Na_2B_4O_7$. A typical illustration is furnished by the reaction between sodium paratungstate and potassium nitrate, which is represented by

$$Na_{10}W_{12}O_{41} + 14\,KNO_3 \rightarrow 5\,Na_2WO_4 + 7\,K_2WO_4 + 7\,N_2O_5.$$

Since both of the substances which are concerned in such reactions are solid at ordinary temperatures, it is necessary to raise the temperature of the mixture to the point at which one or both of them is partly or wholly fused in order to insure complete interaction; hence the factors which determine the reversibility of such reactions are the same as those which determine the reversibility of the reactions considered in the preceding paragraph. As most of the processes of this class can be carried out by heating a known weight of the sample with a known weight of the reagent in an open crucible they are extremely simple and in many cases extremely accurate.

CHAPTER XI

DETERMINATION OF WATER IN GYPSUM

I. Facts Upon Which the Determination Is Based

Composition of Gypsum. The composition of this mineral is represented by the formula $CaSO_4 \cdot 2\,H_2O$. It is frequently found in the form of colorless, transparent and beautifully crystalline masses, which are practically free from other minerals and mechanically occluded impurities of all kinds, and which contain the theoretical percentage of water.

Conditions Necessary for Complete Dehydration. When a small amount of gypsum is placed in a loosely-covered vessel and the latter is slowly heated very little water is driven off until a temperature of 102° is reached, and even if kept at this temperature for a week only three-fourths of the water present in the sample is lost by it. These facts indicate that under these conditions the reaction

$$2\,(CaSO_4 \cdot 2\,H_2O) \rightarrow (CaSO_4)_2 \cdot H_2O + 3\,H_2O$$

has been completed and also that the partial pressure of the water vapor, which is in equilibrium with both the di-hydrate and the hemi-hydrate of calcium sulfate, slightly exceeds atmospheric pressure at 102°. If the temperature of the vessel is still further increased the remainder of the water present in the sample is slowly driven off when a temperature of 160° is reached, indicating that under these conditions the reaction

$$(CaSO_4)_2 \cdot H_2O \rightarrow 2\,CaSO_4 + H_2O$$

has been completed.

The rate at which both of these transformations take place under the conditions specified is very low and it is necessary to use a temperature of at least 180° if it is desired to completely expel the water from gypsum by heating in a loosely-covered vessel. Since the only other decompositions involving a change of weight which can result from a change in temperature produce either calcium oxide or a basic sulfate of calcium, and sulfur trioxide and since neither of these changes begins to take place until a temperature of at least 600° has been reached, there is no objection to using a temperature much higher than 180°.

Properties of Anhydrous Calcium Sulfate. Two forms of calcium sulfate are known; one of these, the so-called "soluble anhydrite," is formed when gypsum is heated to moderate temperatures only, and is both more soluble and much more hygroscopic than the "insoluble anhydrite." When gypsum is dehydrated below 500° it is difficult to weigh the residual salt accurately, owing to the speed with which it takes up water vapor from the atmosphere. The difficulty can be avoided by heating in a vessel, which can be closed by means of a tightly-fitting stopper, and since ordinary glass does not begin to soften until a temperature of 400° is reached, a glass weighing bottle can be used for the determination, altho it must be heated and allowed to cool slowly to prevent it from cracking. Satisfactory results can also be obtained by heating in a covered porcelain or platinum crucible, but some experience is necessary to weigh the residual salt with sufficient speed to prevent slight errors due to the slow absorption of water.

The difficulties can also be avoided by using the absorption method, that is, by collecting and weighing the liberated water, but this requires a more elaborate apparatus and takes more time.

Possible Sources of Error. If gypsum is heated rapidly it sometimes shows a tendency to "boil," that is, the sudden conversion of the chemically combined water into steam rends the larger masses into extremely fine particles, and this may lead to

an appreciable mechanical loss. The difficulty can be avoided entirely by heating slowly until most of the water is expelled, preferably in a deep vessel and by reducing the size of the particles of which the sample is composed. Care must be taken, however, to avoid long-continued grinding, as it has been shown that this may result in the loss of appreciable amounts of water, probably owing to the heat developed by friction.

II. Details of Method of Procedure

Preparing and Weighing Out Sample. Crush several grams of the air-dry sample in a clean mortar until the resulting grains are about the size of a pin head, and transfer to a clean, dry "sample tube"; that is, a test tube about 1 cm. in diameter and 8 cm. long, which is provided with a good cork stopper.

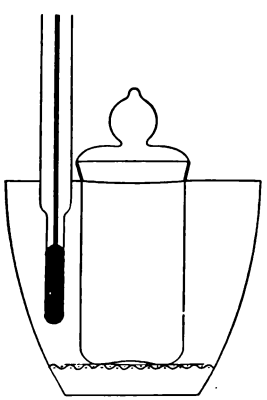

Fig. 21. — Apparatus for Determination of Water

Procure a weighing bottle of not more than 20 cc. capacity, clean carefully and wipe both inner and outer surfaces with a dry cloth, then allow to stand, preferably in the balance room, for twenty minutes or until it has taken up the normal amount of moisture from the air. Weigh the bottle and cover accurately to within 0.5 mg. Remove the cover, and add about 2 gm. of the prepared sample, and again cover and weigh accurately to within 0.2 mg.

Dehydration. Procure a nickel crucible of some 50 cc. capacity, cut a circular piece of wire gauze slightly larger than the bottom of the crucible, ignite it over a flame, and place in the crucible as shown in Fig. 21. Cut a piece of asbestos cloth of slightly smaller size and place on top of the gauze. Support the crucible on a piece of wire gauze which is placed some two inches above the top of a Bunsen burner, then remove the cover from the weighing bottle and place the bottle

inside the crucible. Heat the gauze with a low flame for ten minutes, then gradually increase the gas supplied until the wire gauze under the muffle is heated to dull redness, and keep at this temperature for a half hour, but do not let the gas take fire and burn above the gauze. The temperature attained inside the muffle should be about 250°; it can be measured by means of a mercury thermometer suspended as shown in the figure.

Weighing the Residual Salt. Shut off the gas, place the cover in position and allow the muffle to cool for about three minutes, then transfer the bottle to a piece of paper, wood or some poor conductor of heat; and after a few minutes, place in the balance room and allow to remain for twenty minutes. If the hot bottle is brought into contact with a piece of cold metal or any other good conductor of heat it is certain to crack. Weigh the bottle to within 0.2 mg.; if it shows any tendency to increase in weight while on the balance pan allow it to stand for another ten minutes and again weigh. Finally place the bottle in the muffle, heat as before for ten minutes, and again cool and weigh. If the difference between the two weighings does not exceed 0.3 mg. the dehydration of the sample can be assumed to be complete. Calculate the percentage of water present.

III. Further Details Regarding the Analysis

Meaning of Percentage Error. In discussing the accuracy of quantitative processes care should be taken to distinguish between "percentage error" and what will be designated in this book as "departure." Percentage error always means the error for every one hundred parts of the substance determined; departure, the difference between the correct percentage and the percentage reported. Thus, if a substance contains exactly 70 per cent of a certain constituent and 69.8 is found by analysis, the departure is $70 - 69.8 = 0.2$, but the percentage error is $100\ (70 - 69.8) \div 70 = 0.285$. The difference between departure and percentage error becomes zero when the substance analyzed contains 100 per

cent of the constituent reported. In general the percentage error of a quantitative process should be expected to increase somewhat as the percentage reported on decreases, but in neither case is the one change proportional to the other.

Accuracy of Method. The determination outlined above represents an ideal quantitative process, as regards both simplicity and accuracy. The entire estimation can be made within two hours, and the results should not differ from the theoretical figure by more than one-tenth of a per cent if the work is carefully executed. The accuracy of the method can be still further increased by increasing the amount of sample used, altho the time needed for complete dehydration is thereby increased.

IV. Questions and Problems. Series 2

1. If the result obtained in this determination is 20.80 instead of 20.93, what is the percentage error? If the same percentage error was made in determining the water in a salt containing 60 per cent of water, what result would you obtain?

2. If 2 gm. of the sample were used in making the determination as directed and the only errors involved were a plus error of 1 mg. in weighing the empty bottle and a plus error of 0.2 mg. in weighing the bottle and residue after ignition, what departure would be obtained? If the only errors involved were a plus error of 0.2 mg. in weighing the empty bottle, and a plus error of 1 mg. in weighing the bottle and residue, what departure would be obtained?

3. What weight of water is present in 1 liter of air saturated at 50° and 760 mm., assuming that the partial pressure of water vapor at this temperature is 92 mm., that a liter of water vapor at 0° and 760 mm. weighs 0.803 gm. and that water vapor obeys the laws of Boyle and Gay Lussac?

4. What are the partial pressures of water vapor, oxygen, and nitrogen in a mixture if the total pressure is 760 mm., and one liter of the mixture contains 0.022 gm. of H_2O, 0.8796 of N_2 and 0.2665 of O_2?

5. If 2 gm. of gypsum are heated to 70° in an open flask, which has a volume of 500 cc., how much gypsum would be left and how much of the hemi-hydrate formed, assuming that the dissociation pressure of gypsum at this temperature is 161 mm., that no water is expelled from the flask, that the water vapor is uniformly distributed in it after equilibrium has been

established, and that one liter of water vapor at 70° and atmospheric pressure weighs 0.641 gm.? *Ans.* 1.5676 gm. left.

6. What difficulties would you anticipate if the method used for the determination of water in gypsum was used for the compounds $CaCl_2 \cdot 6\,H_2O$, $Mg(NO_3)_2 \cdot 6\,H_2O$, $FeSO_4 \cdot 7\,H_2O$, $ZnSO_4(NH_4)_2SO_4 \cdot 6\,H_2O$?

7. If 1 gm. of a mixture which contained $CaCO_3$ and $SrCO_3$ lost 0.15 gm. when heated to 900°, and .1292 gm. when heated from 900° to 1200°, what percentages of the two carbonates were present? (For data see page 83.)

8. What methods might be used to determine the water in a mixture of a hydrated salt, which was known to give a dissociation pressure of 200 mm. when heated to 300°, and a carbonate, which was known to give a dissociation pressure of 400 mm. when heated to the same temperature?

9. Show why you are justified in neglecting the error from buoyancy in the determination of water in gypsum, assuming that only brass weights are used, that the specific gravity of brass is 8.33, that of gypsum is 2.32, and that of anhydrous calcium sulfate is 2.964.

CHAPTER XII

DETERMINATION OF WATER IN CRYSTALLIZED COPPER SULFATE

I. Facts Upon Which the Determination Is Based

Purification of the Salt. When copper sulfate is purified by recrystallization the pentahydrate alone separates since the vapor pressure of the solution is greater than that of this hydrate even if the temperature of the saturated solution used reaches a value of 50°. The separated crystals should be dried by pressing them between folds of filter paper, and preserved in stoppered bottles at a temperature not in excess of 25°. The salt sold by reliable dealers as chemically pure usually contains very nearly the theoretical percentage of water.

Conditions Necessary for Dehydration. Although the vapor pressure exerted by even the monohydrate of copper sulfate at 100° exceeds the partial pressure of water vapor normally present in the atmosphere, experience shows that the last traces of water are driven off from this salt very slowly at this temperature. As the salt does not begin to decompose further until a temperature of 341° is attained, there is no objection to dehydrating at 200°, at which temperature all of the water is rapidly and completely expelled. The anhydrous salt is extremely hygroscopic, and altho the method used for the determination of water in gypsum can be employed in this case also the more widely applicable absorption method will be described here.

The Efficiency of Different Dehydrating Agents. The accuracy of the absorption process for the determination of water depends upon the efficiency of the reagent used to absorb the liberated water vapor. The activity of all such reagents depends

upon their capacity to combine with water, and is large in proportion as the dissociation pressure of the compound formed by the addition of water is small.

Phosphorus pentoxide is the most powerful dehydrating agent known, which is due to the fact that the water-vapor pressure of the phosphoric acid formed is practically zero. As it is obtained in the form of a fine white powder, whose surface rapidly becomes coated with an impervious layer of phosphoric acid, and as it is an expensive reagent, its use is avoided except when an unusual degree of dehydration is necessary.

Concentrated sulfuric acid owes its power to the formation of a series of liquid hydrates, which are miscible with water in all proportions. The vapor pressure of the concentrated acid is but little less than that of phosphoric acid; that of the diluted acid increases rapidly with the dilution. It has been measured for a wide range of concentrations at a number of temperatures and the data obtained is extremely useful for the preparation of dehydrating reagents of specified power. The gas to be dehydrated can be passed thru tubes, which are designed to hold the acid in liquid form, or thru U-tubes containing pieces of pumice stone saturated with it; the acid in such tubes must be renewed frequently.

Calcium chloride forms a series of hydrates, all of which are extremely soluble. It is to be had from dealers in two forms. The "fused" salt is almost anhydrous, and is dense and heavy; the "granular" reagent, if fresh, contains from 15 to 20 per cent of water, and is light and porous. Its dehydrating power decreases as its water content increases. Samples containing from 14 to 24 per cent of water ($CaCl_2 \cdot 1$ to $2\ H_2O$) yield a vapor pressure of 0.54 mm.; those containing from 24 to 40 per cent ($CaCl_2 \cdot 2$ to $4\ H_2O$) yield a pressure of 1.47 mm.; those containing from 40 to 50 per cent ($CaCl_2 \cdot 4$ to $6 \cdot H_2O$) yield a pressure of 2.47 mm. The vapor pressure of the fused salt should be less still, but its action is much slower than that of the lower hydrates, and its efficiency may not be greater unless the gas to be dehydrated is passed over

it very slowly. Altho the granular reagent is a less efficient dehydrating agent than concentrated sulfuric acid the fact that it can be obtained in the form of a light porous solid makes it more convenient to use.

The Use of Granular Calcium Chloride. If the partial pressure of the water vapor in the air passed thru the apparatus during the determination is not equal to or less than the vapor pressure of the dehydrating agent used to retain the water separated from the sample being analyzed, the result may be increased by water taken up from the air. If the air passed thru the apparatus is dehydrated by the same reagent that is used to absorb the water liberated from the sample no such error should result. Under these conditions also no error should result from the use of a dehydrating agent, which fails to remove the last traces of water from the air passed thru the absorbing tubes since both tubes should reduce the concentration of the water vapor to the same value, and the amount of water taken up by the second absorbing tube represents the increase in the concentration of water vapor produced by the decomposition of the sample under analysis.

Conditions Necessary for Complete Absorption. If the liberated water vapor is drawn thru the absorbing tube too rapidly some of it may not be retained. If the air current used is not made to pass continuously in the proper direction some of the liberated water vapor may find its way into the absorption tube thru which the air enters. A steady and continuous stream of air can be drawn thru the apparatus at any desired rate by the use of an "aspirator bottle" (E of Fig. 22). If air enters the apparatus at any point except thru the tube designed to purify it, the moisture which it contains may be absorbed and weighed with the separated water. Hence the joints of the apparatus must be tight, but since the pressure inside and outside of the apparatus need not differ much, no difficulty should be experienced in making them so.

The time needed for the determination depends largely upon

the amount of air which must be passed thru the apparatus to free it from water vapor before the sample is heated, and also to wash the separated water vapor into the absorption tube after the sample has been decomposed; it increases, therefore, with the capacity of the apparatus, which should be made as small as possible.

II. Construction of the Apparatus

Procure and fit together the parts of an apparatus similar to that shown in Fig. 22 as follows:

For *A* procure a simple U-tube about 18 cm. in length. Clean and dry it carefully and fill with lumps of dry granular calcium

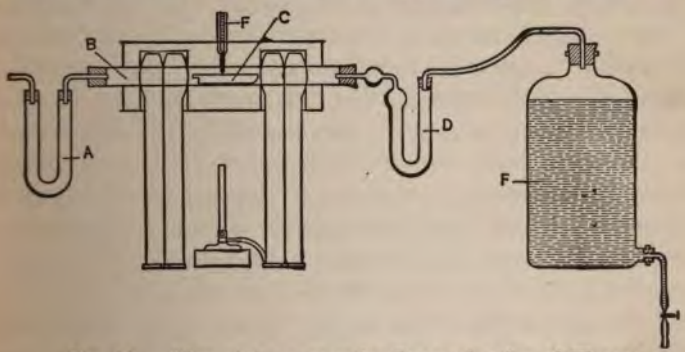

Fig. 22. — Plan of Apparatus for Determination of Water

chloride of about the size of a pea. Place small wads of cotton on top of the reagent in both limbs and insert in the two ends well-fitting cork stoppers provided with an inlet and outlet tube respectively. Prepare also two "plugs" by inserting short pieces of glass rods into pieces of rubber tubing of slightly smaller internal diameter, and use to cover the inlet and outlet tubes, and thus protect the reagents from deterioration when the tube is not in use.

For *B* procure a piece of either hard or soft glass tubing about thirty centimeters long, the diameter of which is sufficient to permit the insertion and removal of the porcelain boat *C* without

difficulty. The sharp edges at the end of the tube should be rounded off by heating in a flame until they begin to soften. Procure two rubber stoppers which fit the ends of the tube snugly and are bored with holes for the admission of the tubes connecting with *A* and *D*.

For *D* procure a smaller U-tube, preferably of the Marchand form, in which one limb of the tube is sealed directly to an inlet tube of smaller diameter, the latter being bent at right angles and provided with a bulb-like enlargement near the middle of the horizontal portion. This bulb serves to condense and retain a large part of the water vapor passing thru the tube, which can be poured out, or removed by a shred of filter paper after the tube has been used; it increases the number of determinations that can be made with it without renewing the absorbing reagent.

Clean and dry the tube, heating it in an air bath if necessary to expel the last traces of water. Insert a small wad of cotton just below the inlet tube, and fill with pieces of granular calcium chloride; then introduce a good cork stopper, which is provided with a narrow outlet tube, into the open limb. Place a few small pieces of sealing wax upon the top of the cork, and melt these by means of a piece of hot metal till the cork and the joint between it and the glass are covered uniformly and smoothly. Prepare well-fitting plugs, by which the inlet and outlet tubes can be covered, and a support of nickel or aluminum wire by which the tube can be suspended.

For *E* procure an aspirator bottle of about two liters capacity provided with an exit tube which can be easily opened or closed by means of a screw pinchcock.

For *F* procure a thermometer capable of indicating temperatures of 300°.

III. Details of Method of Procedure

Preliminary Operations. Prepare the sample by crushing several grams of the dry crystalline salt to a fine powder in a clean agate mortar and placing in a clean, dry sample tube.

Ignite the porcelain boat by holding it in the flame of a burner, slightly above the apex of the inner blue cone, for a few minutes, then place in a desiccator until perfectly cool, which should require about twenty minutes, and weigh accurately to 0.2 mg. Next add to the boat about 1 gm. of the sample and again weigh accurately.

Wipe the Marchand tube with a clean dry cloth, place it in the balance room for twenty minutes, then weigh with the two plugs in position accurately to within 0.2 mg. If the tube appears to gain in weight while on the balance pan it must be allowed to stand longer, that is, until the weight is constant.

Assembling the Apparatus. Connect the larger U-tube with the combustion tube by means of a rubber stopper. Fill the aspirator bottle with water, attach it directly to the other end of the combustion tube and allow about 200 cc. of water to flow out rather rapidly, that is, within a period of about ten minutes.

Disconnect the aspirator and place the porcelain boat and contents in the combustion tube at the point indicated in the figure. Connect the Marchand tube with the combustion tube by means of the rubber stopper, taking pains to press it firmly into place. Connect the aspirator with the free end of the Marchand tube and adjust the pinchcock until the water flows from it at a rate of about five drops per second, and maintain this rate of flow during all the subsequent operations.

Decomposing the Hydrate. Light the burner under the muffle, and allow the temperature as shown by the thermometer to slowly rise to about 100°, and maintain it as near this figure as possible for twenty minutes. This should expel four-fifths of the water somewhat rapidly; decrepitation may take place but does no harm as the residue is not to be weighed. Some of the water may condense in the colder portions of the tube just outside of the muffle and it may be necessary later to heat that part of the tube slightly, by changing the position of the muffle, but this must be

watched carefully, or small amounts of water vapor or sulfur may be expelled from the rubber stopper.

Next increase the height of the flame and allow the temperature to gradually rise to 200° and maintain between 200° and 250° for twenty minutes longer. At the expiration of this period the residue in the boat should be of a dead white or slightly gray color; if it shows a tinge of blue the heating should be continued longer.

Weighing the Liberated Water. Disconnect the aspirator, remove the Marchand tube and cover the inlet and outlet with the proper plugs, place in the balance room and weigh as before. Remove the porcelain boat by means of a small wire hook and disconnect and cover the ends of the larger U-tube. Calculate the percentage of water present.

IV. Questions and Problems. Series 3

1. Would you expect the sulfates of sodium, zinc, aluminum and iron, respectively, to decompose into the corresponding oxides at higher or lower temperatures than the sulfate of copper?

2. Ten liters of moist air measured at 20° are passed thru a tube filled with calcium chloride containing 45 per cent of water, then thru a tube filled with calcium chloride containing 18 per cent of water, what weight of water might be taken up by the latter tube? *Ans.* 0.019 gm.

3. A saturated solution of Na_2HPO_4 is placed in a desiccator, which also contains a large vessel filled with 65 per cent sulfuric acid and is kept at 30°. If the vapor pressure of the acid is 7 mm., the dissociation pressure of $Na_2HPO_4 \cdot 12\ H_2O$ is 26 mm., that of $Na_2HPO_4 \cdot 7\ H_2O$ is 18 mm., that of $Na_2HPO_4 \cdot 2\ H_2O$ is 2 mm., what changes would take place in both solutions? What difference might it make if the volume of the Na_2HPO_4 solution was large and that of the H_2SO_4 solution small?

4. How could you prove that copper sulfate formed a hydrate having the formula $CuSO_4 \cdot 3\ H_2O$?

5. Calculate the probable formula of a hydrate of magnesium sulfate which was found to contain 64.2 per cent of water

6. Show how the data given by Fig. 17 enables you to determine whether heat is absorbed or liberated during this determination.

CHAPTER XIII

DETERMINATION OF CARBON DIOXIDE IN LIMESTONE BY THE EVOLUTION METHOD

I. Facts Upon Which the Determination Is Based

Choice of Method. The value of a sample of limestone for many purposes is determined by the percentage of carbon dioxide which it contains. This determination can be made by ascertaining the loss which takes place when a known weight is ignited in a crucible, but this method is inaccurate if the sample also contains chemically combined water or organic matter. When these substances are present the determination can be rapidly made by the evolution method with an alkalimeter; the use of the Bunsen alkalimeter (see Fig. 23) will be described here. The results obtained by this method should not differ from the correct figure by more than .2 per cent.

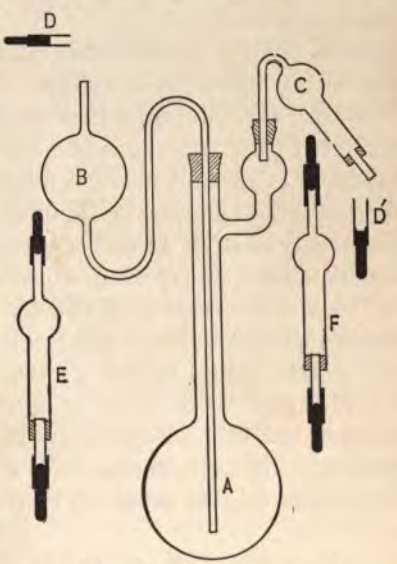

Fig. 23. — Bunsen's Alkalimeter

Possible Sources of Error. The errors involved in weighing a Bunsen apparatus are necessarily somewhat large owing to variations in the amount of hygroscopic water which condenses

on its surface, they should be made as small as possible by using a counterpoise as suggested on page 21. The use of a large amount of sample reduces the effect of this error; as much as 2 gm. can be used to advantage.

The carbon dioxide liberated in the Bunsen apparatus is saturated with water vapor which must be absorbed before the gas is permitted to escape. Calcium chloride can be depended upon to remove all but a trace of water from the escaping gas, provided the escaping gas is not passed thru the absorbing tube too rapidly. Some samples of calcium chloride contain small amounts of calcium oxide and therefore absorb carbon dioxide; hence the calcium chloride in the tube *C* should be saturated with carbon dioxide before it is used.

Altho the reactions between the carbonates found in limestone and either dilute hydrochloric or sulfuric acids are practically complete, the solution which remains after the decomposition is saturated with carbon dioxide, and to this extent the separation of the latter is incomplete. If a moderate excess of dilute hydrochloric acid is used and the residual solution heated slowly to about 50° practically all of the dissolved carbon dioxide is expelled, and there is little danger of expelling either acid or water vapor.

The specific gravity of carbon dioxide is greater than that of air and the gas retained and weighed with the apparatus after use will weigh slightly more than that present in it before use, unless a sufficient amount of air is drawn through it, after the decomposition has been completed. This air should be dehydrated by passing it thru the drying tube *E*, otherwise the moisture which it contains may be taken up by the drying tube *C*.

II. Preparation of the Apparatus

Carefully clean the three parts *A*, *B* and *C* of a Bunsen apparatus (see Fig. 23), by rinsing with acid if necessary, then with water allowing them to drain and then wiping the outer surfaces dry with

a clean cloth. Dry the inner surface of the tube *C* by heating either in an air bath or very cautiously over a wire gauze.

Charge the drying tube by placing a small wad of cotton in its enlarged end, filling to within 1 cm. of the other end with lumps of dry, granular calcium chloride of about the size of a pea, covering with a second wad of cotton, and closing with a cork of the proper size, which is provided with an inlet tube of small diameter. Press the cork into the tube till flush with its end and cover with a little sealing wax. Pass carbon dioxide from a generator thru the tube for about twenty minutes and displace the excess by means of a current of air.

III. Details of the Method of Procedure

Charging and Assembling the Apparatus. Prepare a long narrow sample tube, which is small enough to pass into the flask *A*, by sealing up one end of a piece of thin-walled glass tubing with a flame and closing the other with a cork, and charge with about 2 gm. of the sample. Weigh the tube accurately and deliver its contents without loss into the bottom of the flask *A*, then withdraw the sample tube and again weigh accurately.

Pour about 15 cc. of dilute hydrochloric acid into a small beaker, insert the shorter of the two tubes attached to the reservoir tube *B* into the acid and suck up about 10 cc. of the acid, then remove the tube *B* and invert, so that the shorter tube again stands above the acid. Carefully remove the acid which adheres to the shorter tube by means of narrow shreds of filter paper.

Next unite *A*, *B* and *C* as shown in the figure, place the plugs *D* and *D'* over the two open ends, let the apparatus stand for a half hour in the balance room and weigh accurately, using a 200 cc. flask, which has also stood in the balance room during the previous half hour, as a counterpoise.

Decomposing the Sample. Remove the plugs *D* and *D'* and set aside where they can not be mixed with the plugs belonging to *E* and *F*. Now cause the acid to siphon over, drop by drop,

from *B* into *A*, controlling the flow by holding the finger against the end of *B* and preventing any of the liberated gas from escaping through the reservoir tube. When all of the acid has been drawn into *A* and when the decomposition seems to be complete, which should take about 15 minutes if the sample has been finely ground, heat the bulb *A* slowly over a wire gauze until the solution attains a temperature of about 50°. Next connect the free ends of the apparatus with the tubes *E* and *F*, attach the latter to an aspirator, and draw 1500 cc. of air thru the apparatus, which should require about 20 minutes. Disconnect the tubes *E* and *F* and replace with the plugs *D* and *D'*, let the apparatus stand for a half hour in the balance room and weigh as before. Report the percentage of CO_2.

IV. Questions and Problems. Series 4

1. Assuming that the capacity of the Bunsen apparatus is 50 cc., that the weight of a liter of air under the prevailing conditions is 1.2 gm., while that of carbon dioxide is 1.84 gm., how large a departure would be made in a determination of carbon dioxide in 2 gm. of pure sodium carbonate if only half the carbon dioxide was displaced by air before the final weighing was made?

2. What other determinations might be made with a Bunsen apparatus?

3. Assuming that the available air space of the Bunsen apparatus was 50 cc. and that of the absorption tube was 10 cc., calculate the volumes of air which should be passed thru the apparatus to reduce the carbon dioxide left after the decomposition to 1 mg., assuming first, that all the air used is uniformly mixed with the carbon dioxide present and second, that none of it is so mixed. *Ans.* 59.46 and 6570 cc.

4. If it was found that 1 gm. of a sample consisting of a mixture of sodium carbonate and sodium bicarbonate yielded a loss of 0.46 gm. in a Bunsen apparatus, what percentage of Na_2CO_3 and $NaHCO_3$ must have been present? (For the method of solving see page 78.) *Ans.* 58.69 and 41.31 per cent.

5. If an error of 0.2 mg. was made in making the determination indicated in the last problem, how large an error would appear in the results of the calculation?

CHAPTER XIV

DETERMINATION OF CARBON DIOXIDE IN BAKING POWDER BY THE ABSORPTION METHOD

I. Facts Upon Which the Determination Is Based

Composition of the Sample. The essential constituents of these mixtures are starch, bicarbonate of sodium, and some reagent which has weakly acidic properties, such as potassium bitartrate, alum or the acid phosphate of calcium. The addition of water to such mixtures brings the active reagents into contact with each other and results in the liberation of carbon dioxide, and since their efficiency as leavening agents depends upon the volume of gas which they liberate under the conditions of actual usage, the available rather than the total carbon dioxide is usually determined. The weight of gas liberated when the sample is treated with water and heated can be determined with an alkalimeter, but the equally accurate absorption method, which has been more generally used, will be described here. The starch, which is added to preserve the mixture, does not affect the method except by producing a pasty mass when heated with water.

Properties of Soda Lime. The substance known as "soda lime" is prepared by adding calcium oxide to a strong hot solution of sodium hydroxide; on cooling, this mixture forms a solid friable mass, which can be broken into pieces and packed into U-tubes. This reagent has the property of rapidly absorbing water vapor, carbon dioxide and other gases which possess acidic properties, with the liberation of appreciable amounts of heat. Absorption of carbon dioxide takes place most rapidly and completely if the reagent is not absolutely dry. As the lumps of reagent used

rapidly acquire an impervious coating of calcium carbonate, which prevents further absorption from taking place, it is advisable to pass the gas thru two tubes filled with the reagent and to determine the resulting increase in the weight of both. Tubes whose volume does not exceed 25 cc. are more efficient, and more accurately weighed than those of greater capacity. A tube of this size when properly charged should weigh about 25 gm., and will absorb at least 1 gm. of carbon dioxide.

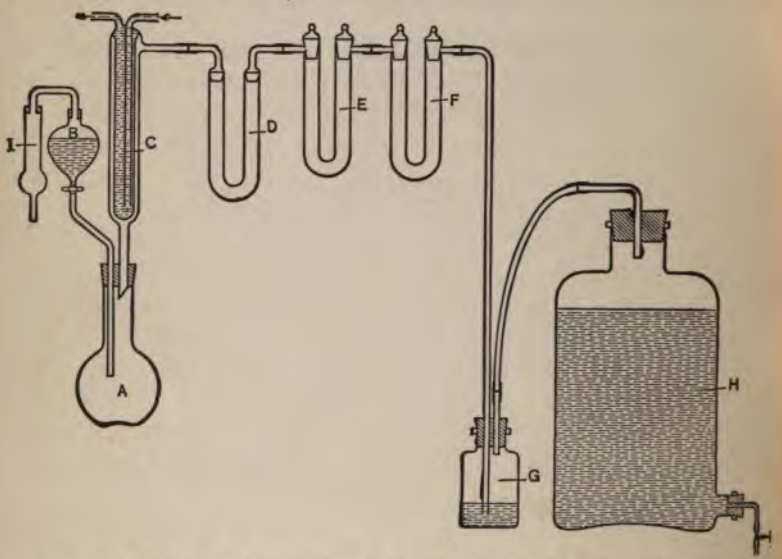

Fig. 24. — Plan of Apparatus for Determination of Carbon Dioxide

II. Construction of the Apparatus

Prepare and set up the apparatus represented in Fig. 24. *A* is the decomposition flask of about 125 cc. capacity; *B* is the acid reservoir, which consists of a separatory funnel of about 40 cc. capacity; *C* is a condenser of the Hopkins form; *D* a glass-stoppered drying tube filled with calcium chloride; *E* and *F*

glass-stoppered U-tubes of about 25 cc. capacity filled with soda lime; *G* a small wash bottle, which indicates the rate at which air is drawn thru the apparatus; *H* an aspirator and *I* a soda-lime tube which removes the carbon dioxide from the air drawn thru the apparatus. The stopper of the flask *A* should be of rubber, and the absorption tubes should be provided with wire loops by which they can be suspended from a horizontal support when in use, and from the balance beam when being weighed.

III. Outline of Method of Procedure

Preliminary Operations. Clean the parts, *A*, *B* and *C*, by rinsing with acid if necessary, then with water and allowing them to drain. Clean the tubes *D*, *E*, *F* and *I* and dry by wiping them as dry as possible and then drying in an oven. Fill the tube *D* with lumps of calcium chloride not exceeding a pea in size, then pass dry carbon dioxide from a generator thru it for about ten minutes and displace the latter by air. In like manner fill the tubes *E*, *F* and *I* with soda lime.

Assemble the various parts of the apparatus and test for leaks by first closing the free end of the tube *I* with a plug, and opening the pinchcock on the delivery tube of the aspirator; if water continues to flow from the aspirator indefinitely, test each joint successively until the leak is found and stopped.

Charging the Apparatus. Disconnect the aspirator, the wash bottle and the soda-lime tubes *E* and *F* and close the latter by turning the stoppers. Wipe the two tubes with a dry cloth, let them stand in the balance room for a half hour and weigh them both separately, using a glass counterpoise. Remove the flask *A* from the apparatus, wipe it dry and add to it from a sample tube about 2 gm. of the sample, being careful to prevent any of it from coming into contact with the side of the flask, then again weigh the sample tube. Close the stopcock of the separatory funnel and charge the latter with about 30 cc. of water. Connect the reaction flask

A, the soda-lime tubes *E* and *F* and the wash bottle with the rest of apparatus.

Making the Decomposition. Allow the water to run into the flask *A* by cautiously opening the stopcock for very short time intervals, endeavoring to produce a slow and uniform liberation of the gas. After all of the water has been introduced, attach the aspirator, remove the plug from *I* and by carefully regulating the aspirator draw a slow current of air through the apparatus. Next start the water running thru the condenser and heat the solution very slowly to the boiling point, then allow the flask to cool very slowly, keeping a steady stream of air passing thru the apparatus.

After 4 liters of air have been passed thru the apparatus, which should take about forty minutes, disconnect the two soda-lime tubes and weigh as before. Calculate the percentage of CO_2 from the increase in the weight of these tubes.

IV. Questions and Problems. Series 5

1. Calculate the volume of CO_2 measured at 25° and 760 mm. liberated by 1 gm. of a sample which contains 12 per cent of available carbon dioxide.

2. Assuming that air contains 0.04 per cent by volume of CO_2 and that 2 liters of air are passed thru the apparatus, what result would be obtained in this determination if the soda-lime tube I was not used, assuming that the correct per cent of CO_2 is 12?

3. A sample of baking powder which is known to contain only starch, $NaHCO_3$ and $C_4H_5KO_6$ (potassium bitartrate) in equivalent proportions yields 12 per cent of CO_2. What is its composition?

4. One gram of a mixture consisting of $CaCO_3$ and $PbCO_3$ is found to contain 0.25 gm. of CO_2. What percentages of CaO and PbO must be present?

5. A sample which contains potassium nitrate is analyzed by weighing out 1 gm., adding 3 gm. of sodium paratungstate ($Na_{10}W_{12}O_{41}$) and heating to constant weight in a crucible. If the crucible shows a loss of 0.3 gm., what percentage of potassium nitrate was present? *Ans.* 56.16 per cent.

CHAPTER XV

DETERMINATION OF MERCURY IN AN ORE

I. Facts Upon Which the Determination Is Based

Decomposition of Mercuric Sulfide. The ores of mercury which are of commercial importance contain the element as the sulfide, that is, the minerals cinnabar or metacinnabarate, or as metallic mercury; they rarely contain more than a small percentage. If mixed with finely divided iron filings and heated the sulfide is decomposed according to a reaction represented by:

$$HgS + Fe \rightarrow FeS + Hg.$$

At a temperature of 100° metallic mercury gives a vapor pressure of 0.27 mm., at 300° the pressure is 246 mm.; hence it is not surprising to find that this reaction can be made complete by heating the mixture to a temperature of 300° in an apparatus one part of which is kept at a temperature which does not exceed 100°, that is, by condensing the vapor as it is formed.

Condensation of Mercury Vapor. The most satisfactory device which can be employed for the retention of the mercury condensed in such an apparatus takes advantage of the tenacity with which mercury attaches itself to plates of gold, silver or copper, which is in part due to the ease with which it forms amalgams with these metals. When mercury vapor condenses on such plates it forms a thin film or series of fine drops, and altho they can be dislodged by brushing or vigorous shaking no difficulty is experienced in accurately determining the weights of mercury adhering to such plates. After weighing, the mercury can be expelled

by heating to a temperature of about 400°; if plates of gold or silver are used their weights remain practically constant; if a plate of copper is used its weight increases slightly, owing to oxidation.

Form of Apparatus Used. Although several forms of apparatus which are based upon the facts cited have been suggested, one devised by Whitton,* which is represented in Fig. 25, is the best. It consists of an iron retort *A* of 24 cc. capacity, a sheet of silver foil *C* about 0.2 mm. thick, a brass dish *B* which is kept full of water, an iron shield which protects the foil from the flame used to heat the retort, and a clamp *D* by which the retort, foil and dish are held together. The silver plate used is about 5 cm. square, and weighs about 2.3 gm.; it can be used for twenty or more determinations, but after repeated use seems to become porous, so that some of the mercury may pass thru it.

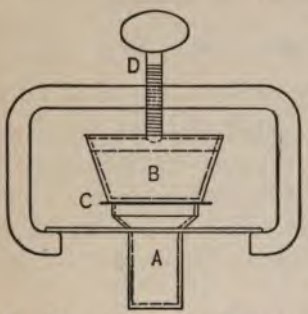

Fig. 25. — Whitton's Apparatus for Determination of Mercury

Sources of Error. As the total volume of air expelled from the retort during the heating should not exceed that due to the expansion of the air originally present, and the maximum concentration of this air with respect to mercury vapor should not exceed that of air saturated at 100°, the total loss from this source should not be large.

As mercuric sulfide is itself appreciably volatile, a relatively large volume of iron filings should be used to insure complete decomposition. The ore and filings must also be carefully dried and the latter washed with gasolene or ether to remove any grease with which they may be contaminated. The maximum amount

* Mineral Industry, **17**, 751 (1908). Apparatus can be procured of Braun-Knecht-Heinmann of San Francisco.

of mercury which can be safely retained by a plate of the size given is 0.07 gm., and the amount of ore used for the determination must be chosen with this statement in mind. It is obvious that great care should be used in weighing the foil.

The temperature to which the retort is heated, and the length of time it is heated in order to insure complete decomposition, must be ascertained by experimenting with pure mercuric sulfide or ores of known composition. When the flame of an ordinary Bunsen burner is used, and the retort is so placed that the flame covers the bottom and reaches a point one-half inch above the bottom, heating for 20 minutes is found to give good results.

An entire determination can be made within an hour and the method is peculiarly adapted to the analysis of low-grade ores, since a large amount of sample can be used.

II. Outline of Method of Procedure

Prepare a plate of silver foil by polishing with a piece of fine emery or crocus cloth, wiping with a clean cloth, drying for a few minutes over a flame and weighing with the greatest attainable accuracy. Weigh out about 5 gm. of iron filings, which are dry and free from grease, and place in the retort. Weigh out on a watch glass a sufficient amount of the dry ore to contain from 20 to 70 mg., and transfer to the retort. Mix the ore and filings very thoroughly with a glass rod, and cover the mixture with another gram of filings.

Place the foil between the retort and water cooler, clamp all three together and support on an iron ring stand above a burner so that the top of the burner is about one and one-half inches below the bottom of the retort. Fill the cooler with water, light the burner, and adjust the gas supply until the flame runs up the sides of the retort for not more than one-half an inch, which should heat the water to boiling in 7 minutes. Renew the water in the dish as it evaporates and after 20 minutes remove the flame and allow to cool for 20 minutes, then disconnect the apparatus,

remove the plate and weigh accurately. Report the per cen mercury.

Expel the mercury from the silver plate by holding it with mercury-coated side uppermost, several inches above the flam a burner, until fumes are no longer given off, and the plate sho faint red glow, but avoid using a temperature which would mel

III. Questions and Problems. Series 6

1. What weight of mercury is present in one liter of air, which has a perature of 100° and is saturated with mercury vapor, if the partial pres of mercury vapor is 0.27 mm.? *Ans.* 0.0023 g

2. If a retort which contains 24 cc. of air at 20° is heated to 300° and expelled air is cooled to 100° before escaping, what volume is expelled?

3. If the retort referred to is charged with 0.1 gm. of pure HgS and proper amount of iron filings and heated to 300°, and if the air and mer vapor are cooled to 100° before escaping, what weight of mercury is di off? What is the percentage error of the determination resulting from cause? *Ans.* 0.04 per ce

4. Derive the simplified expression representing the application of Law of Mass Action to the reaction used in this determination.

5. What objections are there to determining mercury by the evol method, that is ascertaining the loss in weight of the vessel in which the rea between mercuric sulfide and iron is made to take place?

6. Would you expect this method to be affected by the presence of Ca FeS_2, As_2S_3, ZnO or $CaSO_4 \cdot 2H_2O$, and if so how?

7. Derive the simplified expression representing the application of the of Mass Action to the reaction which takes place when mercuric oxi heated, assuming first, that none of the mercury formed is condensed liquid and second, that some of it is condensed to a liquid.

SECTION III

GRAVIMETRIC PRECIPITATION PROCESSES

CHAPTER XVI

GENERAL THEORY OF PRECIPITATION PROCESSES

quilibrium and Solubility. All precipitation processes in-
re the formation of a new solid phase from a liquid phase, and,
efore, heterogeneous equilibrium. The new solid phase may
lt from the addition of a reagent which changes the physical
perties of the solvent and reduces the solubility of the con-
uent which separates, or from a chemical reaction brought
ut by the addition of a reagent, or from the action of a galvanic
rent. Since the concentration of the substance precipitated, in
solution from which it separates, cannot exceed that of a satu-
ed solution of this precipitate, the completeness of those reactions
ich result in the formation of precipitates is determined by the
ibility of the precipitate. The solubility at ordinary temper-
res, expressed in milligrams per liter of solution, of some of
precipitates frequently used in quantitative analysis is given
the following table.*

Cl	2.0	$Ca(COO)_2$	5.6
Br	0.13	$CaSO_4$	2004 0
I	0.0025	CuI	0.43
CNS	0.02	$PbSO_4$	44.0
$_2CrO_4$	25.0	$PbCrO_4$	0.2
$_2O$	25.0	$SrSO_4$	100.0
CO_3	18.6	$Sr(COO)_2$	46.0
SO_4	2.3	.....	.....

* Most of the figures given here have been calculated from the data sum-
rized in the Landolt-Börnstein, Physikalische-Chemische Tabellen.

The Solubility of Electrolytes. Let us represent the total solubility of a binary electrolyte, such as silver chloride, expressed in moles per liter by m and its degree of dissociation in this solution by x. Then mx represents the concentration of the dissociated electrolyte and also that of the anion and cation; also $m\ (1 - x)$ represents the concentration of the undissociated electrolyte. If the dissociation of the electrolyte obeys the mass law the relation between the concentrations is expressed by the equation

$$(mx)^2 = k \cdot m\ (1 - x).$$

In the solution under consideration both $m\ (1 - x)$ and $(mx)^2$ are constant and since both bear a simple relation to the total solubility either could be used as a measure of the total solubility. Since the electrolyte here concerned is a slightly soluble salt, its dissociation can be considered to be practically complete, and hence the value of mx corresponds to that of its total solubility, expressed in moles per liter, and the value of $(mx)^2$ is therefore easily determined. This value has been designated by Ostwald by the term "solubility product"; it is one of the constants frequently used in discussing quantitative processes.

When a precipitate results from a chemical reaction, an excess of the reagent used is invariably added, and the concentration of either anion or cation which enters into the formation of the precipitate must exceed the concentration of the anion or cation in a solution of the precipitate which contains no other substances. In discussing the effect of other substances upon the solubility of such electrolytes it was assumed by Nernst that "In any saturated solution of a slightly soluble electrolyte the concentration of the undissociated electrolyte, and also the product of the concentrations of the ions into which it dissociates, are constant." These theorems merely assert that the values which represent the concentrations of the undissociated electrolyte and the solubility product in solutions obtained by saturating water with the pure electrolyte are true for *all* solutions of that electrolyte, that is,

are not affected by the presence of other substances. If they are true the addition of an excess of the precipitating agent must decrease the solubility of the precipitate.

Theory of the Precipitation of Silver Chloride. Let us assume that we precipitate the chlorine in 200 cc. of a 0.2 molar solution of sodium chloride by the addition of silver nitrate in solid form, in order to avoid changing the dilution. If we first add an exactly equivalent amount, that is, 0.04 mole of the silver salt, the ratio of the silver salt added to salt present is 1, and the mixture must contain equal concentrations of Ag and Cl ions. One liter of water saturated with AgCl contains 0.002 gm., and the concentration of the solution in moles is $0.002 \div 143 = 1.39 \times 10^{-5}$. This also

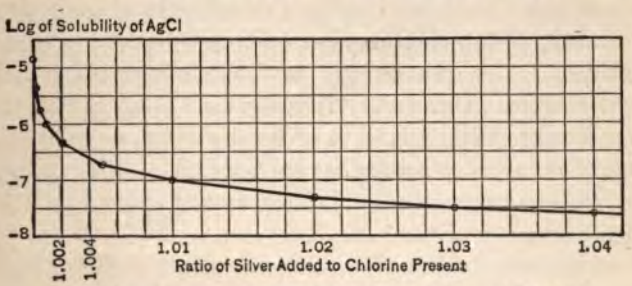

Fig. 26. — Changes in the Solubility of Silver Chloride

represents (Ag^+) and (Cl^-) and its square, that is, 1.9×10^{-10}, the solubility product.

Let us now add 0.0002 mole of $AgNO_3$, which will increase (Ag^+) to slightly more than 0.001 and will change the ratio of silver added to salt present to 1.005. If we assume that both sodium chloride and silver nitrate are completely dissociated this addition must change (Cl^-) to $1.9 \times 10^{-10} \div 0.001$, or 1.9×10^{-7}, that is, a very slight increase in the amount of reagent used reduces the solubility of the precipitate enormously. The relation between solubility and amount of reagent used is shown in the curve represented in Fig. 26, in which the abscissas represent the ratios of silver salt to

sodium chloride, and the ordinates the logarithm of the solu
It is important to note that the rate at which the solubi
reduced decreases very rapidly as the value of the ratio is
from 1. It is also evident that if sodium chloride is used
precipitation of silver from a silver salt, exactly the same re
in solubility must be effected by the addition of an am
sodium chloride which makes the ratio of sodium chloride
salt the same as the ratio of silver salt to sodium chloric
points represented on the curve. The precipitate has a m
solubility when this ratio has the value 1.

Factors Which Affect the Theory. Ideal conditions ha
assumed in the preceding paragraph. The dissociation
precipitate and added salt has been assumed to be compl
the formation of complex ions has been entirely disregarc
attempting to test the theory by comparing calculate
observed changes in solubility it is scarcely possible to maintain such conditions. The solubility of most of the precipitates tabulated on page 111 is so small that the experimental error involved in determining the change in solubility resulting from the addition of a slight amount of the added salt is large. Hence in most of the investigations made, either relatively soluble precipitates have been used, or the concentration of the added salt has been made large. In the former case the dissociation of the precipitate, and in the latter case the dissociation of the added salt cannot be considered complete, and it becomes necessary to ascertain and make use of the degree of dissociation of the electrolytes in calculating the change in solubility concerned. These values cannot be determined by a direct measurement in solutions which contain more than one electrolyte, and all attempts to calculate them from the experimental data involve assumptions whose validity can be questioned. In spite of these difficulties many results have been obtained which agree fairly well with the predictions of the theory, others show wide variations from them.

In some cases also the formation of complex ions may render

the results of such calculations valueless. It seems necessary to assume that all ions, especially those which possess a slight degree of affinity for their charges, show a variable tendency to increase this affinity by taking up undissociated molecules from the solution. The large number of double salts which can be prepared, and which can be assumed to result from the combination of such ions with others of opposite sign, support this statement. This tendency for the formation of complex ions increases with the concentration of the electrolyte taken up; it is responsible for two effects which are of importance in quantitative analysis. In some cases it leads to the formation of precipitates of abnormal composition, as shown in the chapter on occlusion; in others it increases the solubility of a precipitate thru the formation of complex ions, which makes it possible for the solution to attain a higher concentration of the constituent which is being separated than would be possible if the simpler ions only were present.

For example, it was found that the solubility of silver choride* in a solution containing 0.933 mole of sodium chloride per liter was 8.6×10^{-5}, that is, more than six times as great as its solubility in pure water, which was explained by assuming that such solutions contain ions of the formula $\overline{AgCl_3}$ and $\overline{\overline{AgCl_4}}$.

Altho some chemists entirely reject one or both of the fundamental assumptions of Nernst, it is now generally believed that the results of all the calculations based upon them are limiting values toward which the actual values converge in proportion as the ideal conditions which they assume are realized; that is, where the concentrations are so small that the dissociation of the electrolytes concerned is complete and the nature of the ions is such that no complexes are formed. This view has been adopted thruout this book.

The use of these principles in calculating the changes in the solubility of precipitates, such as $PbCl_2$, which dissociate with

* Forbes, Journ. of Amer. Chem. Soc., **33**, 1186 (1911).

the formation of one or more bivalent ions, presents no theoretical difficulties. Since, however, such salts dissociate in stages, solutions of them may contain appreciable concentrations of intermediate ions, such as $PbCl^+$, and it is less probable that the ideal conditions referred to can be realized than when salts of a simpler type are concerned.

Theory of Separation of Two Closely Related Ions. The possibility of separating two ions by the addition of a reagent which is capable of forming slightly soluble compounds with both can be discussed with advantage from the standpoint of the theory already elaborated. Let it be assumed that silver nitrate is slowly added to a solution containing equivalent concentrations of potassium iodide and potassium chloride. Silver iodide must begin to separate as soon as the product $(Ag^+) \times (I^-)$ exceeds S, where S represents the solubility product of silver iodide, and silver chloride must begin to separate as soon as the product $(Ag^+) \times (Cl^-)$ exceeds S', where S' represents the solubility product of silver chloride. As more silver nitrate is added, more silver iodide separates, and (I^-) is progressively reduced. Since, further, the solution remains saturated with respect to silver iodide, and S is constant, the concentration of the silver ions must progressively increase. Both of these changes will continue until (Ag^+) has become so large that the solution is also saturated with respect to silver chloride. At this point

$$(Ag^+) \times (I^-) = S, \quad \text{and} \quad (Ag^+) \times (Cl^-) = S'.$$

Since both these expressions relate to the same solution (Ag^+) has the same value in both, and hence

$$\frac{(I^-)}{(Cl^-)} = \frac{S}{S'}.$$

This expression tells us that the condition for saturation with respect to both compounds is that (I^-) shall bear the same relation to (Cl^-) that S bears to S'. If still more silver nitrate is added

further quantities of both silver iodide and silver chloride must separate, but the relation of (I^-) to (Cl^-) must remain constant. The solubility product of silver iodide can be calculated from the data given on page 115 to be 1×10^{-16}, and that of silver chloride to be 1.9×10^{-10}. Therefore the condition for saturation with both salts is

$$\frac{(I^-)}{(Cl^-)} = \frac{1 \times 10^{-16}}{1.9 \times 10^{-10}} = \frac{5.3 \times 10^{-7}}{1}.$$

That is, the concentration of the iodide ions must be reduced to $5.3 \times 10^{-7} \times (\bar{Cl})$ before precipitation of the chlorine ions can begin to take place.

If, further, it is assumed that one equivalent of silver is added for every equivalent of iodine present, the concentration of both iodine and silver would be $\sqrt{1 \times 10^{-16}}$, or 1×10^{-8}, and hence the maximum concentration of chlorine ions which could be present without causing some silver chloride to separate would be $(1 \times 10^{-8}) \div (5.3 \times 10^{-7})$, or 0.019; that is, if the concentration of $\bar{Cl}$ reached the value 0.019 and if one equivalent of silver was added for every equivalent of iodine present, the solution would be just saturated with both precipitates. It is clear that an accurate separation of the iodine from solution which contains both iodine and chlorine ions would not be possible except within certain narrow limits. Obviously one equivalent of silver would have to be added for every equivalent of iodine present if the precipitation is to be even approximately complete, but even if no excess were used some silver chloride would separate if the concentration of the chlorine ion exceeded 0.019.

The separation of two ions which yield precipitates with the same reagent is scarcely possible unless the solubilities of these precipitates differ by large amounts, and even then the amount of reagent used must be properly adjusted to the concentrations of the two ions present.

CHAPTER XVII

FILTERING, WASHING AND IGNITING PRECIPITATES

Media Used for Filtration. The separation of precipitates from liquids is essentially a process of straining, in which solid particles are separated from liquid particles by the use of a porous diaphragm. A variety of media which differ greatly as to their efficiency and adaptability to different purposes are employed for such separations.

Cellulose made into the form of paper of a loose, open texture has many advantages; it should represent the purest possible form of this substance, and is, therefore, digested with both hydrochloric and hydrofluoric acids and washed very carefully before use, for the purpose of reducing the percentage of inorganic salts present to a minimum. It is not appreciably dissolved or otherwise affected by solutions of salts or by acids and bases of moderate concentration, but is attacked by strong solutions of acids and bases, and cannot be used for the filtration of such solutions. The papers made from it for quantitative separations differ greatly as to thickness and texture; those of an open and porous character permit very rapid filtration, but are unable to retain very fine precipitates; the more compact varieties are more efficient but slower.

Asbestos or mineral wool, unlike cellulose, is non-combustible; it should not be appreciably hygroscopic. Different grades of the mineral vary greatly as to their freedom from associated minerals, length of fiber, and the ease with which they can be reduced to a satisfactory pulp. The best is the pure white long-fibered variety, which can be easily reduced to a pulpy mass by triturating with

water in an agate mortar. It is customary to digest with strong hydrochloric acid before use in order to remove any impurities present which might be dissolved during its use as a filter and thereby change its weight, or contaminate the resulting filtrate. It is not readily made into a fabric which can be used like paper, but must be supported on a plate or disk of platinum or porcelain, which is provided with a number of fine holes (Witt filter plates), or on a crucible the bottom of which is similarly provided.

Glass wool is used in the same manner as asbestos. As the fibers of which it is composed are more elastic and pack together less compactly than asbestos it is not so readily made into a filter of equal efficiency.

Platinum sponge, which is easily made by reducing the salts of that element to the metallic state, is also used like asbestos but is too expensive for any but certain special purposes.

Alundum, or fused aluminum oxide, which has been crushed to a fine powder, can also be made into an efficient filter. It is usually mixed with a small amount of cementing material and molded into the form of crucibles or cylinders. It is not appreciably affected by treatment with even strong acids or strong alkalies.

Devices for Filtering When the Precipitate Is Not To Be Weighed. In discussing the devices used in filtration we can distinguish between those cases in which the precipitate is to be weighed at once, and those in which the separation is only one of the preliminary operations which precede the final separation of the desired substance. In the latter case the precipitate may be discarded entirely, or it may be again brought into solution by treatment with other reagents, and the desired substance can be separated from the resulting solution by further operations. Two classes of devices are usually employed in such cases. The first and simplest consists of a paper filter supported on a glass funnel. The rate at which a liquid passes thru such a device depends, aside from the character of the filter paper, upon the nature of the precipitate and the viscosity of the liquid filtered. It

can be greatly increased by lengthening the funnel stem, that is, by attaching to the latter a piece of glass tubing, which is bent to form a complete turn near its upper end and is slightly constricted at its lower end as represented in Fig. 27. If the paper is accurately fitted to the funnel and the outlet of the stem is small enough to prevent air from entering, the tube gradually fills with liquid and the pressure exerted by the liquid assists in drawing further quantities of it thru the filter. If the tube is made too long the pressure may be great enough to break the paper at the apex of the funnel as it is unsupported at that point; hence it is often necessary to introduce a support in the form of a cone made of very thin platinum foil and provided with a number of fine openings or of a small piece of linen cloth folded to fit the apex of the funnel.

Fig. 27. — Funnel for Rapid Filtration

Fig. 28. — Filtering Tube and Suction Flask

Whenever a paper filter is used some of the precipitate, especially if the latter is finely divided, is carried into the interior of the paper, and when it is desired to bring this precipitate into solution or to treat it with other reagents a large volume of reagent must be poured thru it, or the entire filter must be opened out and digested in a separate vessel. This often consumes much time, requires the use of an undesirably large volume of reagent and increases the total volume of the solution to an undesirable amount; also the cellulose of the filter may be attacked by the reagent which it is desired to use.

These difficulties are all avoided by the use of an asbestos filter such as is shown in Fig. 28, in which a Witt filter plate is used in the bottom of a "filtering tube." In this and all devices in which asbestos pulp is used, suction greater than that easily obtained by increasing the length of the stem of the funnel is necessary. In the device shown in the figure the filter tube is attached to a closed filter flask by means of a rubber stopper, and the flask is attached thru its side neck to a Bunsen pump or some other suction device. It permits of extremely rapid filtration and by varying the thickness and fineness of the asbestos layer, precipitates of any desired fineness can be retained. After the filtration has been completed the filter and adhering precipitate can be readily and completely transferred to another vessel, and treated with any desired reagent, even with strong bases or acids, after which the residual asbestos can be removed by a second filtration.

Devices for Filtration When the Precipitate Is To Be Weighed. If the precipitate is to be weighed it must be freed from water and other adhering substances, and often must be strongly ignited before it can be accurately weighed. It is extremely desirable, therefore, that the medium used for the filtration shall have such properties, that it can be treated exactly as the precipitate is treated without danger of affecting changes in its weight, and that the filter used shall be of such a form that it can be easily ignited and accurately weighed both before use and after the precipitate has been separated on it.

Cellulose is decidedly hygroscopic and furthermore slowly loses water and carbonizes even at a temperature of 100°, and altho it is sometimes considered necessary to weigh a precipitate on a paper filter it should be avoided wherever possible. When this medium is used for filtration it is customary to destroy the entire filter by burning in a good supply of air and to weigh the residual precipitate mixed with the ash of the paper in a crucible. As the ash content of the filter should not exceed .1 mg. it can usually be disregarded.

Asbestos, glass wool and platinum sponge can be ignited strongly

without suffering appreciable changes in weight, and are, therefore, to be preferred to paper in such cases. The most convenient form for a filtering device in which such media are to be used and the precipitate is to be ignited, is that of a crucible of tall form but of moderate size and weight such as is represented in Fig. 29. This is the device first used by Gooch and is usually known as a Gooch crucible. Its bottom is pierced by a number of fine holes and furnishes a support for the media named. It is connected with a filtering tube by means of a rubber band and this tube is attached to a filter flask as shown in the figure.

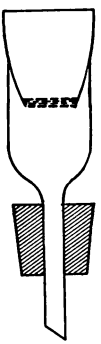

Fig. 29.— Gooch Crucible

A crucible of alundum is equally satisfactory, but since the entire crucible is made of porous material more time and care must be expended in washing the filter free from soluble salts than where the bottom layer only constitutes the filtering medium.

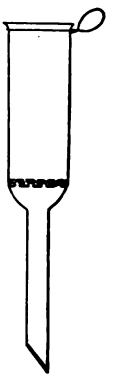

Fig. 30. — Glass Filtering Tube

When it is not necessary to heat the precipitate after filtration to more than 350° a glass filter tube, similar to the one represented in Fig. 30, which is used in conjunction with a Witt plate or platinum cone can be used to advantage.

The Different Classes of Precipitates. All substances which have been separated as precipitates possess certain physical peculiarities, altho these peculiarities may be modified to some extent by varying the conditions of precipitation. They may be roughly classified as follows:

Crystalline precipitates, such as calcium sulfate, calcium oxalate and magnesium ammonium phosphate. They frequently contain water of crystallization and possess a definite crystalline form, which can be recognized by a magnification of about three hundred

diameters. In this type the tendency for the formation of supersaturated solutions, from which the normal amount of precipitate separates but slowly, is most pronounced, and often makes it desirable to make use of mechanical shaking devices when it is necessary to reduce the time needed for the complete separation of the precipitate to a minimum. The solubility of these precipitates is comparatively large, and the addition of special reagents for the reduction of the error from solubility often becomes necessary. They are, however, extremely easy to filter and wash.

Pulverulent precipitates, such as the sulfates of lead and barium, and the phosphomolybdate of ammonium, are composed of spherical or indefinitely bounded particles, which are too small to be recognized as individuals except by very high magnification. The particles are sometimes so fine that it is difficult to retain them on paper filters, unless these are very hard and dense. It is often possible to avoid the formation of such particles by using conditions which make the precipitate separate very slowly, that is, by diluting both the original solution and the added reagent, and by adding the latter slowly and with constant stirring. Long-continued digestion also will frequently increase the size of the smaller grains as explained on page 34. Some precipitates of this class are more satisfactory if separated from a hot, others from a cold solution, and the best conditions of treatment for every precipitate must be learned thru experiment.

Another peculiarity of such precipitates is their tendency to "creep," that is, small amounts of the very fine particles are carried thru capillary action over the sides of the filter and above the liquid which it contains, and where a paper filter is used appreciable amounts may be carried entirely out of the filter and on to the sides of the funnel. The method of treatment adopted, and the presence of certain reagents seems to have some effect on this peculiarity.

Curdy precipitates are very similar to those classed as pulverulent but are peculiar in that the very fine particles of which they

are composed readily coalesce to form curdy masses. This is often spoken of as "coagulation" and can be assisted by heating, violent stirring, and by the presence of certain reagents. This class of precipitates is one of the most desirable, as they are easily and rapidly filtered and washed. The chloride, iodide and cyanide of silver and cuprous sulfocyanate are good examples.

Flocculent precipitates are entirely amorphous and very bulky. They are made up of large aggregates of fine particles, which are normally of a loose flocculent nature, but may become hard and compact if allowed to dry, or if sucked against the bottom of the filter by pressure. Under some conditions, they become slimy or gelatinous, and are then extremely difficult to filter. They are usually separated in the best conditions for filtration if the solution is hot, but long-continued boiling sometimes makes them slimy. They retain soluble salts readily and are hard to wash completely. Ferric hydroxide furnishes a typical illustration.

Gelatinous precipitates, such as the hydroxide of aluminum, are also composed of extremely fine particles which tend to aggregate into jelly-like masses. They are extremely bulky and as they rapidly clog up the pores of the filter are very hard to filter and wash. In general, they are best kept off the filter until nearly all of the liquid present has been passed thru it.

Colloidal precipitates, good examples of which are silicic acid, the sulfide of arsenic and the hydroxide of chromium, are distinguished by their tendency to form "pseudosolutions" or "hydrosols." When treated with water these solids undergo a transformation which results in the formation of a mixture that seems to be a homogeneous solution and readily passes thru a filter, even tho the latter is capable of retaining extremely fine particles. Such mixtures are not homogeneous, for it can be shown by the use of the ultramicroscope that they actually contain solid particles of too small a size to be recognized by the usual methods of magnification. The formation of such pseudosolutions can be entirely prevented by keeping a small concentration of some electrolyte

in the liquid with which they are in contact. As most precipitates are formed in the presence of one or more electrolytes no difficulty is usually experienced in filtering them, but when they are washed with pure water pseudosolutions may form as soon as the concentration of the electrolyte has been sufficiently reduced; the solid which passes thru the filter in this form is usually reprecipitated on coming into contact with the main filtrate.

It becomes necessary, therefore, to wash such precipitates with a solution of some electrolyte. Electrolytes differ greatly in their ability to prevent the formation of pseudosolutions and altho the salts of di- or tri-valent metals are much more efficient than the salts of ammonium the latter are very generally used for this purpose, as they can be entirely volatilized by igniting the precipitate.

The Theory of Washing Precipitates. The precipitate finally separated on the filter is contaminated with various soluble substances present in the solution associated with it. If these substances are easily volatilized during the subsequent ignition, and if they do not react with the precipitate in such a manner as to give rise to volatile compounds with the precipitate during the ignition, their removal is not necessary. In the great majority of cases both of these conditions are not complied with and the precipitate must be washed with an appropriate liquid, the amount of which should be made as small as possible, owing to the solvent action of the liquid on the precipitate.

The efficiency of the method used in washing precipitates is readily calculated if ideal conditions only are considered. If A represents the weight in grams of the impurity to be removed and V the volume in cubic centimeters of the wash solution added, and if it is assumed that the filter is in all cases allowed to drain until only 1 cc. of liquid remains in contact with it, and that there is an equal distribution of the soluble salt thruout the volume of liquid used, each washing would remove $\frac{V}{(V+1)}A$ gm. of the

impurity and leave $\frac{1}{(V+1)}A$ gm. behind. The general expression for the amount of impurity left on the filter after n treatments is $\left(\frac{1}{V+1}\right)^n A$. If, for example, the amount of impurity to be removed was 0.2 gm. and the precipitate was washed four times with 9 cc. of solution under the conditions named above, only 0.00002 gm. would remain, an amount which can be safely neglected.

The formula shows further that the efficiency of the process decreases greatly as the volume of the liquid left in contact with the precipitate increases, and that the use of several portions of wash solutions of small volume is decidedly more effective than the use of a smaller number of large portions. If the 36 cc. of wash solution used in four equal portions in the above example had been used as a single portion the weight of impurity still left in the filter would amount to 0.0054 gm.

Discrepancy Between the Theory and Practice. Experience does not agree with the predictions of the theory outlined above and the assumption that the impurities are equally distributed thruout the wash solution used is not valid. When the latter is merely poured thru the filter it may not remain in contact with the precipitate long enough to bring about a uniform distribution of the soluble salts, and it is often difficult to prevent the formation of channels in the mass of precipitate, especially where the latter is of a gelatinous character, which prevents the solution from coming into intimate contact with the soluble impurities. The only reliable method of procedure is to wash the precipitate until an actual test of the washing shows that soluble substances are no longer being removed in appreciable amounts. It is often convenient to ascertain this by evaporating a reasonably large volume of the last washings (at least 20 cc.), to complete dryness and noting the amount of residue left. In other cases it is more convenient to test the washings for the compound which is being

removed by an appropriate and sufficiently delicate qualitative test. It is usually safe to assume, however, that precipitates which have been brought down under identical conditions from solutions of the same composition require the same amount of washing, and in repeating quantitative processes much unnecessary labor can be avoided by ascertaining the amount of washing necessary in the first determination.

Washing by Decantation. It is desirable to wash precipitates which rapidly clog up the pores of the filter in the original vessel, that is, to avoid bringing them on the filter as far as possible until the impurities have been removed. This can be effected by allowing the precipitate to settle to the bottom of the vessel, "decanting" off the clear supernatant liquid thru the filter, adding wash water, stirring and repeating the same cycle of operations as long as may be necessary. The separation of precipitates of low density is often an extremely slow process, and where they are also bulky, comparatively large amounts of solution must be left in contact with the precipitate after each decantation; on the other hand the wash solution remains in contact with the entire precipitate long enough to insure an equal distribution of the soluble impurity thruout its volume. On the whole the process of washing by decantation is slow but with certain types of precipitate it is the best method to employ.

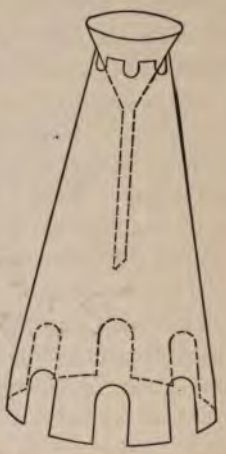

Fig. 31. — Support for Drying Filter

Ignition of Precipitates. The precipitate finally separated is necessarily wet, and must be dried before it can be weighed; frequently it is retained on a paper filter, which must be burned up; and it often consists of a mixture, that must be converted into a compound which has a definite composition. All of these

changes represent gas-evolution processes, and hence precipitation processes involve the use of the principles discussed in Chapter X.

The chief difficulty encountered in igniting precipitates which have been separated on a paper filter is the partial reduction which they may undergo thru the action of the carbon monoxide and volatile hydrocarbons formed during the decomposition of the paper. The difficulty is largely eliminated by adopting the following procedure:

First, the filter is dried at a temperature of 100° or less in order to make it possible to separate the greater part of the precipitate from the filter before it is destroyed. This is conveniently effected by placing the funnel containing it in a support similar to that shown in Fig. 31 and heating on a hot plate or sand bath.

Second, the filter is removed from the funnel, inverted over a clean dry watch glass which rests on a piece of glazed paper, the precipitate detached and transferred to the watch glass without loss by crumpling slightly between the fingers.

Third, the filter is made into a compact roll and dropped into the crucible in which the ignition is to be made, and heated cautiously until all volatile matter has been "smoked off"; the temperature is then raised to redness and the heating continued until the residual carbon is entirely consumed. Obviously these operations should be carried out in a good supply of air and hence the crucible should be supported on the triangle in an inclined position and the flame allowed to play against its bottom only.

Fourth, the precipitate temporarily set aside is transferred without loss to the crucible by means of a camel's hair brush, which requires careful manipulation.

Finally, the crucible is heated under whatever conditions are necessary to convert it into a pure substance of known composition. This may require heating in a current of some particular gas.

CHAPTER XVIII

THE PHENOMENA OF OCCLUSION

Theories Advanced to Explain the Phenomenon. Many precipitates are found to possess the property of retaining certain soluble constituents of the solution from which they have separated in such a form that they cannot be removed, even by long-continued washing. The phenomenon is a complex one; three theories have been advanced to explain it.

Schneider suggested that the soluble salt was taken up by the precipitate as the latter separated, and remained distributed thruout the interior of the solid particles; that is, the phenomenon is the result of the formation of a solid solution in which the precipitate is the solvent and the soluble salt the solute. If this is true we should expect to find definite saturation limits for every precipitate with respect to the occluded substance, but such limits have not been found in most of the cases which have been investigated.

Ostwald designates the phenomenon by the term "adsorption." This term was first used by E. du Bois Reymonds to represent the retention of soluble substances by porous or finely divided solids when placed in solutions containing them. A typical illustration of it is the well-known property of bone-charcoal of removing coloring matter from solutions. According to the theory elaborated by Ostwald an attractive or restraining force is exerted by the solid, which tends to hold the molecules of dissolved substance in the immediate neighborhood of its bounding surfaces, and either delays or entirely prevents the removal of these substances by washing. The action of bone-charcoal seems to be remarkable as the great majority of solids possess this property to a much

smaller degree. Very few precipitates absorb coloring matters, and their ability to retain soluble salts is of a decidedly selective character.

Richards believes that the phenomenon is due to chemical rather than physical forces, and designates it by the term "occlusion." According to this theory complex basic salts or molecular compounds, which are but slightly soluble, are formed to a greater or less extent along with the desired precipitate. Thus the occlusion of ferric salts by barium sulfate is explained by assuming that the latter precipitate is contaminated with small amounts of a double sulfate of the formula $BaSO_4 \cdot Fe_2(SO_4)_3 \cdot H_2O$. When this compound is ignited the ferric sulfate is decomposed, and three molecules of SO_3 and one of water are expelled, and one molecule of $BaSO_4$ and one of Fe_2O_3 are obtained. This explains why the results are too low, when this salt separates with the precipitate, in spite of the fact that it is contaminated with Fe_2O_3. Altho it is probable that solid solution and adsorption are in many instances concerned with the phenomenon in question, it will be designated in this book by the term occlusion.

Occlusion Varies with the Concentration of the Soluble Salt. One of the most important and well-established facts relating to the phenomenon is that the amount of occlusion increases as the concentration of the salt in the solution from which the precipitate separates increases, but is not proportional to that concentration. Some experiments on the occlusion of nitrates by barium sulfate illustrate this statement. In these experiments 25 cc. of a solution of sulfuric acid containing exactly 0.425 gm. of H_2SO_4, which should, therefore, yield exactly 1.0118 gm. of $BaSO_4$, were used. Variable amounts of potassium nitrate were added in the different experiments, but the solution was in every case diluted to exactly 200 cc., heated to boiling, and the $BaSO_4$ precipitated by the addition of 50 cc. of a solution containing 1.3 gm. of $BaCl_2$; after standing for sixteen hours the precipitate was filtered off, washed thoroughly, ignited and weighed. The results were as follows:

Series No.	1	2	3	4
Wt. of KNO_3 present	0.0000	0.2000	1.0000	5.0000
Wt. of ppt. found (*A*)	1.0131	1.0199	1.0308	1.0476
Wt. of ppt. found (*B*)	1.0134	1.0160	1.0291	1.0468
Average of *A* and *B*	1.0133	1.0180	1.0300	1.0472
Excess of wt. found	0.0015	0.0062	0.0182	0.0354

A qualitative examination showed that the precipitates obtained in the first series contained very slight amounts of chlorides, those obtained in the other series gave a slight alkaline reaction. It is probable that the 1.5 mg. in excess of the theoretical weight obtained in the first series represents occluded barium chloride, the much larger excesses obtained in the other series represents barium oxide, which resulted from the decomposition of barium nitrate occluded by the precipitate. The last three series of experiments show clearly that the amount of occlusion increases with the concentration of potassium nitrate, but is not proportional to it.

Occlusion Takes Place While the Precipitates Separate. A second well-established fact is that occlusion takes place especially during the time the precipitate is separating from the solution. This was shown by a fifth series of experiments, which were carried on exactly as those of the third series except that the 1 gm. of potassium nitrate was added after the precipitant had been added and the mixture had been allowed to stand for ten minutes. The weights obtained were 1.0140 and 1.0144 gm. respectively. These figures show that the occlusion of the nitrate was very small if added after the precipitate had separated from the solution. Some experiments are on record which show that barium sulfate and other precipitates do occlude soluble salts even after they have separated from the solution, but to a very slight extent only.

Occlusion Varies with the Method of Precipitation. A third factor which has a pronounced effect upon the amount of occlusion

is the concentration of the precipitant used, and the manner in which it is added. If a solution of barium chloride is added to a solution of sulfuric acid the latter will in general be in excess in the resulting mixture up to the time at which an equivalent amount of barium chloride has been added; if a solution of sulfuric acid is added to a solution of barium chloride the latter will in general be in excess up to the time at which an equivalent amount of sulfuric acid has been added. The former set of conditions will favor the occlusion of sulfuric acid, the latter of barium chloride. As barium chloride is occluded more readily than sulfuric acid, and further is not appreciably volatilized on ignition whereas sulfuric acid is completely volatilized, the method of procedure first named might be expected to yield lower results than the one named last. This was shown in a sixth series of experiments in which the conditions of the first series were maintained except that the sulfuric acid, diluted to 200 cc. was added to the barium chloride, diluted to 50 cc. The results obtained were 1.0249 and 1.0212. In series 1, owing to the dilution of the solution to which the precipitating agent was added, occlusion of sulfuric acid was small and was more than counterbalanced, that is, to the extent of 1.5 mg., by the occlusion of barium chloride. In the sixth series, on the contrary, the occlusion of sulfuric acid was reduced to a minimum, while the occlusion of barium chloride was at a maximum and hence the average result was nearly 12 mg. too high.

It should be noted that it is impossible to insure an absolutely uniform distribution of the precipitating agent thruout the mixture during the time it is being added. There is a pronounced tendency for the concentration of both reagents to exceed temporarily the average concentration of the entire mixture at certain portions of the solution. For this reason, some of the precipitate may separate in the presence of a much greater concentration of one reagent or the other than corresponds to its average composition, and the effect of mixing the two reagents in the predetermined order may be greatly diminished. These difficulties may be

largely avoided by using dilute solutions, by adding the precipitant very slowly, and by stirring vigorously while it is being added. Complete separation of the precipitate also requires an appreciable time interval, and if the rate at which it separates is less than that at which the reagent is added, much of the precipitate may separate in the presence of an unduly large concentration of the reagent. In the experiments described above the barium chloride was added during an interval of ten seconds, and altho the mixture was stirred vigorously while the reagent was being added, even in experiment 1 an excess of 1.5 mg. was obtained. The actual amount of chloride occluded by the precipitate included not only the excess of 1.5 mg. but also the normal deficiency due to the solubility of the precipitate, which probably represented 1 or 2 mg. more. It could have been greatly reduced by adding the precipitant more slowly and by reducing the excess added. This was actually shown to be the case in a seventh series of experiments in which the precipitations were made under the same conditions as the first series, excepting that the precipitant was added drop by drop during an interval of twenty minutes. The weights obtained were 1.0102 and 1.0095.

Owing to the extreme difficulty of obtaining absolutely identical conditions with respect to these factors decided differences in the amount of occlusion may result, even where the attempt is made to carry out the determinations under parallel conditions. This is largely responsible for the variations which appear in some of the series of experiments here described; these variations are especially large where the total amount of occlusion is also large.

What Salts Are Occluded. Certain ions are largely occluded, others to a slight extent only. This is shown in the following series of experiments, which were made under the same conditions as the first series, excepting that amounts of chlorides on the one hand and of nitrates on the other sufficient to yield equal concentrations of Cl and NO_3 ions, respectively, were introduced into the solution before precipitation.

Series No.	8	9	10	11
Salt added	0.0000	0.37 HCl	0.59 NaCl	0.75 KCl
Wt. of ppt. *A*	1.0131	1.0135	1.0088	1.0054
Wt. of ppt. *B*	1.0134	1.0143	1.0103	1.0064
Avg. *A* and *B*	1.0133	1.0139	1.0096	1.0059
Error	+0.0015	+0.0021	−0.0022	−0.0059

Series No.	12	13	14	15
Salt added	0.54 $(NH_4)Cl$	0.56 $CaCl_2$	0.48 $MgCl_2$	0.0000
Wt. of ppt. *A*	1.0080	0.9954	1.0140	1.0136
Wt. of ppt. *B*	1.0091	0.9961	1.0155	1.0137
Avg. *A* and *B*	1.0086	0.9958	1.0148	1.0137
Error	−0.0032	−0.0160	+0.003	+0.0019

Series No.	16	17	18
Salt added	0.63 HNO_3	0.85 $NaNO_3$	1.0 KNO_3
Wt. of ppt. *A*	1.0376	1.0368	1.0308
Wt. of ppt. *B*	1.0400	1.0413	1.0291
Avg. *A* and *B*	1.0388	1.0391	1.0300
Error	+0.0270	+0.0273	+0.0182

Series No.	19	20	21
Salt added	0.8 $(NH_4)NO_3$	0.82 $Ca(NO_3)_2$	0.73 $Mg(NO_3)_2$
Wt. of ppt. *A*	1.0244	1.0144	1.0339
Wt. of ppt. *B*	1.0238	1.0174	1.0330
Avg. *A* and *B*	1.0241	1.0159	1.0335
Error	+0.0123	+0.0041	+0.0217

By comparing the entire series of results in which chlorides were present with the series in which equivalent concentrations of nitrates were present it is apparent that the substitution of NO_3 for Cl ions increased the total weight of precipitate found by an proximately equal amount. The very high results obtained en even moderate amounts of most of the nitrates used were sent are evidently due to the fact that the precipitates contained ates in addition to $BaSO_4$, probably as the result of the forma-

tion of complex compounds. It is not improbable that the SO_4 ions possess an appreciable tendency to unite with electrically neutral $Ba(NO_3)_2$ molecules and that the complex ion formed unites with Ba ions to form a salt of the formula $BaSO_4 \cdot Ba(NO_3)_2$, or that the solution contained small concentrations of ions having the formula $\overset{+}{Ba}\overset{+}{N}O_3$ which combined with $\overline{\overline{SO}}_4$ to form $(BaNO_3)_2SO_4$.* The probability of such reactions as these would be determined for the most part by the solubility of the hypothetical compound, as compared with that of $BaSO_4$. The occlusion of chlorides may be due to an analogous series of reactions, but the tendency for these reactions to take place is decidedly less.

A further study of these results indicates that there are decided differences in the extent to which the metallic ions represented are occluded. The introduction of sodium, potassium, ammonium and calcium ions reduces the positive errors resulting from the presence of equivalent concentrations of chlorine and nitrate ions necessarily added at the same time, and when chlorine is the anion added these negative errors exceed the positive ones and the net results are low. The probable explanation is in all cases the presence of compounds similar to $BaSO_4 \cdot Na_2SO_4$, that is, the formation of double salts in which a metal having a smaller atomic weight than that of barium is substituted for that element.

The results obtained in the experiments in which hydrogen and magnesium ions were added are not so conclusive. In general there is a very slight increase in the weights of precipitates obtained, but these increases are not far from those that might properly be attributed to the chlorine and nitrate ions also added at the same time. Some work done by other experimenters has shown that the presence of moderate concentrations of hydrogen ions gives slightly low results, probably owing to the formation of an acid sulfate of barium.

Methods of Avoiding the Error from Occlusion. It is impossible to predict to what extent a given substance will be occluded

* Hulett and Duschak, Zeit. für anorganische Chemie, **40**, 196 (1904).

by a given precipitate and even where the error from this s is known to be large it is difficult to avoid or overcome it.

If the ion in question is occluded but slightly and the solu of the precipitate is very small the error can often be reduc negligible proportions by making the precipitation from a ciently diluted solution. In some cases it is preferable to re the ion which is occluded by an evaporation process, or to re it by another ion which is occluded to a smaller extent by th of a reagent which renders it insoluble, or converts it into a In other cases it is possible to reduce the concentration of th that is occluded by adding reagents which reduce its degr ionization.

In many cases it becomes necessary to purify the precip containing the occluded compound by dissolving and reprecip ing under more favorable conditions, that is, by the proces "double precipitation." The difficulty with this method i find a solvent which dissolves the precipitate readily witho introducing large concentrations of other ions, which are als largely occluded.

CHAPTER XIX

GENERAL THEORY OF ELECTROLYTIC SEPARATIONS

Chemical Changes Effected by the Electric Current. The transmission of an electric current, of a sufficiently high intensity, thru a solution of an electrolyte is associated with physical and chemical changes, some of which can be used to advantage in quantitative analysis.

The chemical effect at the cathode is always some form of reduction. The hydrogen ion here loses its positive charge, and either forms gaseous hydrogen or acts directly as a reducing agent. Certain metallic ions, such as ferric and stannic ions, either first lose a part of their charges and form ferrous and stannous ions, or separate as metals. Certain other metallic ions, such as those of the alkali group, are first reduced to the metallic state, but the resulting metals react with water to form hydrogen and an alkaline hydroxide.

The chemical effect at the anode is always some form of oxidation. The anions of the halogen group are liberated as such and act directly as oxidizing agents. The SO_4 ion decomposes into sulfur trioxide and oxygen, but the former reacts with water and forms sulfuric acid; the NO_3 ion decomposes into nitrogen pentoxide and oxygen, but the former reacts with water and forms nitric acid. The oxygen thus liberated may separate as a gas or may act as an oxidizing agent. Altho in general the simple metallic ions separate as such at the cathode, lead, manganese and thallium ions separate at the anode in the form of insoluble peroxides, especially if the concentration of the hydrogen ions is large.

Metals Which Can Be Determined. Under certain conditions the metals precipitated at the cathode, and the peroxides precip-

itated at the anode adhere to the electrode firmly, and the weight of the metal or oxide precipitated can then be determined readily, if the weight of the electrode is known. The necessity of filtration, which forms a troublesome feature of many quantitative processes is thereby avoided. A large number of factors affect the rapidity and completeness with which the different metals are precipitated, as well as the physical properties and purity of the resulting precipitate. Thus far electrolytic methods have been most successfully applied* to the determination of copper, mercury, silver, antimony, tin, iron, nickel, cobalt, cadmium and zinc as metals, and of lead and manganese as oxides.

The Voltage Needed. If the difference of potential between two electrodes immersed in a solution of an electrolyte is small a barely perceptible current passes thru the solution; if the potential difference is gradually increased a point is finally reached at which the amount of current carried by the solution shows a marked increase, which corresponds to the point at which the ions present first begin to lose their charges. This voltage represents the so-called "decomposition voltage" of the electrolyte concerned. Its value is mainly dependent upon the algebraic sum of the numbers representing the voltages necessary to separate the element or radical composing the anion and cation from their respective charges. It depends further upon the concentration of the solution, the temperature, and to a slight extent upon the size and distance between the two electrodes and the metal of which they are composed. Decreasing the concentration by the factor ten increases the value of the decomposition voltage by $\frac{0.058}{n}$ volts, in which n represents the valence of the ion concerned. It is difficult to determine these values accurately, owing to the large number of variables concerned, and the fact that disturbing

* The literature of electrochemical processes is extensive. Summaries of the more important methods will be found in Edgar F. Smith's Electrochemical Analysis and Alexander Classen's Quantitative Analysis by Electrolysis.

secondary actions often take place. The approximate values of the voltages necessary to deprive some of the more important ions, in solutions of normal concentration, at ordinary temperatures, of their charges are as follows:

Al	Zn	Cd	Fe	Ni	Pb	H	Cu	Sb	Hg	Ag	SO_4
+1	+0.49	+0.14	+0.06	−0.05	−0.13	−0.28	−0.61	−0.75	−1.03	−1.05	+2.18

From this table it is easy to calculate that it would be necessary to maintain a difference of potential greater than 1.57 volts in order to cause metallic copper to separate from a solution containing normal concentrations of Cu and SO_4 ions, but as the copper is deposited the concentration of the copper ions continually decreases, and this necessitates a continuous tho slight increase in the voltage used, if the separation is to be even approximately complete. This fact is not of especial importance unless the solution also contains other metallic ions, which have a slightly greater decomposition voltage. In this case it may be impossible to completely separate one metal without using a voltage which causes the second metal to begin to separate also. In general, only those metals whose decomposition voltages differ by several tenths of a volt can be separated from each other by maintaining a constant voltage during the electrolysis. The addition of certain reagents, such as potassium cyanide, to solutions containing two metals sometimes reduces the concentration of one metallic ion to a greater extent than the other, and makes it possible to carry out the separation by the "constant voltage" method which would otherwise be impossible.

The voltage used also affects the current strength, for according to Ohm's law the strength (expressed in amperes) must equal the tension (expressed in volts) divided by the resistance (expressed in ohms). In a circuit in which electrolysis is being effected the voltage actually available is diminished by the decomposition voltage of the electrolyte decomposed; hence the current strength actually available is represented by the voltage available minus

the decomposition voltage of the electrolyte divided by the resistance of the circuit.

Forms of Electrodes Used. Electrodes of platinum are to be preferred to those of any of the more common metals, since they can be ignited directly in the flame, are not attacked by solutions of acids or alkalies during electrolysis, and can be treated for the removal of the precipitated metal after electrolysis with strong acids. Owing to the cost of the metal the cathode should be as light as possible for the surface exposed; it should also have such a form as to favor circulation of the solution as much as possible; and should be capable of being easily removed from the solution, washed and weighed. Some of the types of electrodes in general use are described below.

The Classen dish represented in Fig. 32 serves to contain the solution being electrolyzed, and is itself made the cathode; the anode used with it is a disk of foil or a horizontally coiled spiral of wire. The size in general use has a capacity of 220 cc. and weighs about 37 gm. This arrangement is not favorable to circulation of the solution; further, the removal of the solution and washing of the precipitated metal is not conveniently carried out. Its chief advantage is that many deposits which, even under favorable circumstances, are but poorly adherent are more easily retained by it without loss than by other forms.

Fig. 32. — Classen Dish and Anode

The Mansfeld electrode shown in Fig. 33 consists of a cylinder of thin foil usually about 5 cm. in length and 2½ cm. in diameter, soldered with gold to a supporting wire. The anode used with it consists of a cylindrically coiled spiral of wire placed in the center of the cylinder, or a horizontally coiled spiral placed at the bottom of the containing vessel. If the former anode is used, that portion of the solution which is surrounded by the cathode is effectively stirred by the currents produced by the gas

liberated at the anode; these currents affect the annular space outside the cathode to a slight extent only, and a much larger percentage of the deposit separates on the inside than on the outside of the cylinder. The unequal distribution of the action of the current over the surface is often shown by the appearance of a spongy deposit on the lower edges of the cylinder, whereas the other portions of the deposit are smooth and adherent. Its efficiency may be greatly increased by drilling a large number of holes in the cathode. If the horizontal form of anode is used the circulation of the solution is more equally distributed but is still very poor.

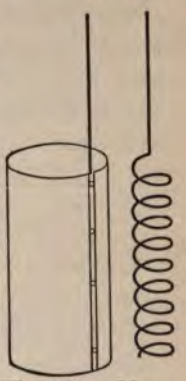

Fig. 33. — Mansfeld Electrodes

The Winkler electrode shown in Fig. 34 consists of a cylinder of fine gauze supported by a wire of small diameter. The form represented is 3 cm. in diameter and 6 cm. in length; the gauze is composed of wires 0.06 mm. in diameter with 41 meshes per linear centimeter. Unlike the Mansfeld form it offers practically no barrier to the circulation of the solution and hence the deposition is much more rapid, and there is comparatively little danger of obtaining spongy deposits.

Fig. 34. — Winkler Cathode

The use of a small amount of mercury, which is placed in the bottom of the beaker or flask containing the solution, and connected with the battery by means of a platinum wire, as a cathode, has been suggested and used to some extent.* It has advantages over the other form of cathodes in the precipitation of metals which give poor deposits or are acted upon by the solution. Its comparatively large weight and the need of great care in washing and

* Jour. Amer. Chem. Soc., **25,** 883 (1903) and **29,** 1445 (1907).

drying before weighing make it less convenient than the other forms.

The comparative efficiencies of the first three electrodes described above are shown in the following table,* which gives their approximate weights, available surfaces and the length of time needed for the precipitation of 0.1975 gm. of copper under identical conditions.

Cathode used	Surface exposed	Weight of cathode	Time required
	Sq. cm.	Gm.	Minutes
Classen dish	100	37	400
Mansfeld cathode	79	11	450
Mansfeld cathode with holes	78	11	390
Winkler cathode	93	4.2	50

Effect of Varying Current Strength. The amount of metal separated from the solution during a given time interval depends upon the rate at which the charges on the electrodes are renewed; that is, upon the quantity of electricity which flows thru the solution during a given time interval. Hence the rate at which the metal is deposited depends upon the current strength, as measured in amperes. The law of Faraday states that the amounts of different metals separated by the same current during the same time interval is directly proportional to their atomic weights and inversely proportional to their valencies. A current of one ampere passing thru a solution of a silver salt for one hour deposits 4.026 gm. of silver and equivalent amounts of other metals. This law might be used to calculate the time needed for complete deposition of all of the metal present if all of the current which passes thru the solution was carried by the electrolyte whose cation is being deposited. Since, however, the concentration of the solution with

* The data quoted in this and the following paragraphs are given in detail in Jour. Amer. Chem. Soc., **32**, 1264 (1910).

respect to the metal which is being determined gradually decreases and must finally become nearly zero, the resistance of the solution and the decomposition voltage must gradually rise and finally reach a point at which other ions begin to lose their charges and take part in the transport of the current. The law of Faraday is valid only when the concentration of the ion which is being deposited is so great that a sufficient number of these ions are within the sphere of attraction of the electrode to neutralize the charges on the electrode. Since circulation of the solution brings these ions into the sphere of attraction of the electrode it favors the deposition of the ions which have smaller decomposition voltages.

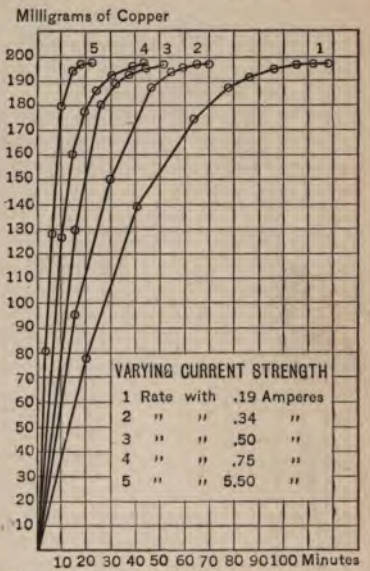

Fig. 35. — Curves Showing Rate at which Copper is Precipitated

The effect of increasing the current strength upon the rate of deposition is illustrated by the curves shown in Fig. 35. The solutions used contained in every case 0.1975 gm. of copper as sulfate, 2 gm. of ammonium nitrate and 4 cc. of concentrated nitric acid, and were diluted to 140 cc. Winkler gauze electrodes were used and current strengths of 0.19, 0.34, 0.5, 0.78 and 5.5 amperes, respectively, were maintained continuously thruout the different experiments.

Increasing the current strength also increases the probability of obtaining spongy deposits, which are difficult to weigh accurately. In some cases this seems to be due to the inability of the metal to form a continuous layer if deposited too rapidly, in others to the fact that hydrogen is deposited to a greater or less extent

with the metal. The maximum current strength which can be safely employed increases in direct proportion to the surface of the cathode available. In expressing the proper conditions for the separation of a given metal it is customary to express the permissible current strength with reference to the so-called "normal density," which represents the ratio between the current used in amperes, and the cathode surface exposed in units of 100 sq. cm. A current of one ampere used with a cathode exposing 100 sq. cm. would represent a normal density of one; doubling both amperage and cathode surface would not affect the normal density; doubling the amperage would double it; doubling the cathode surface would halve it.

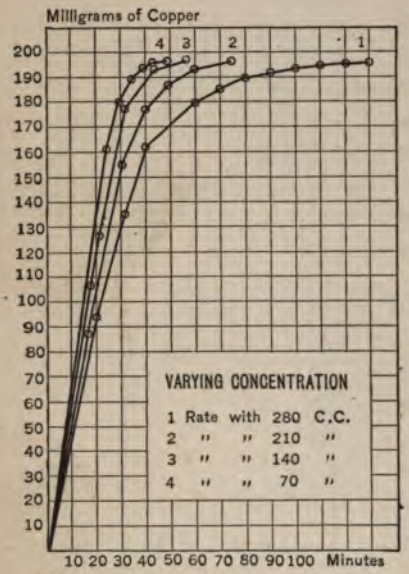

Fig. 36. — Curves Showing Rate at which Copper is Precipitated

Effect of Varying Concentration. The effect of varying concentration on the rate of precipitation is shown by the curves of Fig. 36. The solutions used in these experiments contained 0.1975 gm. of copper as sulfate and were diluted to 70, 140, 210 and 280 cc., respectively. They also contained 1 cc. of concentrated nitric and 2 cc. of concentrated sulfuric acid for each 140 cc. of solution present. A Winkler gauze electrode and a current of 0.34 ampere were used in all experiments.

These curves show that the rate of precipitation decreases rapidly as the concentration decreases, which is partly due to the fact that with the greater concentrations a greater percentage

of the current used was carried by the copper ions than by the hydrogen ions. Since rapid circulation of the solution reduces to some extent the effect of decreasing concentration, and since the circulation of the solution depends upon the convection currents produced by the gases liberated at the electrodes, part of the effect here shown is due to the fact that the larger volumes are less efficiently stirred. It is desirable, therefore, to keep the volume of the solution as small as possible, that is, just sufficient to cover the electrodes.

The Composition of the Solution Used. Since the rate of precipitation depends upon the concentration of the metallic ion which is to be precipitated, the addition of any other salts that are capable of forming complex ions containing that metal should be avoided. The simple nitrates and sulfates are usually to be preferred as electrolytes, owing to their comparatively large dissociation constants. The use of nitrates as electrolytes, and in general the presence of NO_3 ions, has the further advantage of reducing the danger of obtaining spongy deposits, since the hydrogen liberated at the cathode is at once oxidized by the solution and does not contaminate the deposited metal.

The presence of halogen salts in addition to an acid has usually been avoided, unless the concentration of the former is extremely small, since the free halogen which is liberated at the anode may attack the platinum, and the resulting platinum ions, which have a low decomposition voltage, may be precipitated with the desired metal. Further, the presence of halogen ions sometimes results in the formation of spongy deposits. These difficulties can be avoided by the addition of a sufficiently strong reducing agent.

It is often necessary, however, to deposit metals from solutions of their complex salts. Silver gives very poor, crystalline deposits when separated from solutions of its simple salts, but good ones when in the form of double cyanides or oxalates. Iron and zinc are not easily precipitated completely in the presence of even a small amount of an acid, but form double oxalates from which

they are readily precipitated. In all these cases the small amounts of simple metallic ions present are removed by the action of the current, the decrease in the concentration of the simple ions causes the complex ions to break down into simpler ones and ultimately the precipitation is complete.

The addition of an acid to a solution frequently makes it possible to separate one of the metals present in a solution which contains several metals in a pure condition. If the hydrogen ion concentration of such a solution is made sufficiently large and the amperage is kept constant none of the metallic ions having a decomposition voltage greater than that of hydrogen can separate. This is the principle upon which the so-called "constant current" method of separating metals by the electric current is based.

Apparatus for Carrying on a Single Determination at a Time. A special form of stand is needed to support the anode and cathode in the solution, and provide an easy method of connecting the former with the positive and the latter with the negative pole of the battery. Short-circuiting of the current thru the stand is usually avoided by making the central rod supporting the two arms to which the electrodes are clamped out of glass.

The voltage available should be sufficiently high to overcome the counter electromotive force of the electrolyte and the external resistance of the circuit, and yield a current of sufficient strength to deposit the metal within a reasonable length of time. It is further desirable that the voltage available be much greater than that actually needed, for, by introducing a variable resistance or "rheostat" in the circuit, currents of a wider range of strengths are available. These conditions are easily satisfied by the use of a storage battery or a series of galvanic cells which can be depended on to yield an approximately constant voltage for a long period of time. Two storage cells of the usual lead || lead peroxide type which give about 4.4 volts or four Daniell cells suffice for the usual range of determinations made.

In order to determine whether the necessary conditions are being complied with, an "ammeter" showing the current strength should be introduced into the main circuit, and a "voltmeter" showing the difference of potential between electrodes should be connected in a shunt circuit. The proper arrangement of the various parts of the apparatus is shown in Fig. 37.

Apparatus for Carrying on Several Determinations at the Same Time. Altho several solutions may be electrolyzed in the same circuit if a sufficiently large voltage is used, the same

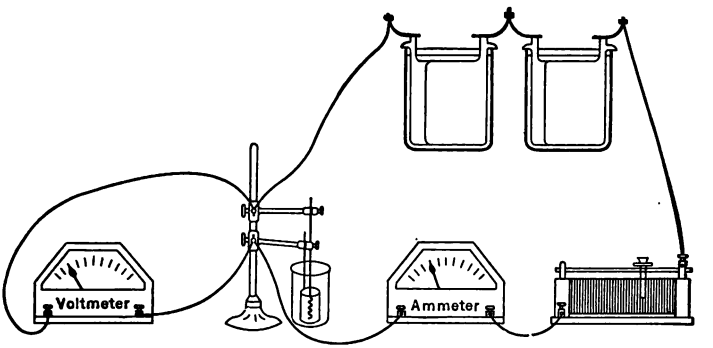

Fig. 37. — Apparatus for a Single Electrolytic Determination

current necessarily passes thru all, and if several different metals are being precipitated it may be impossible to satisfy the proper conditions for each. Furthermore, after precipitation in any of the solutions has been completed, the current must be interrupted while the electrodes are being removed, possibly permitting much of the precipitate in some of the other solutions to redissolve. For these reasons it is necessary to split up the main circuit into as many shunt circuits as there are determinations to be made. If all these solutions offer the same counter electromotive force and resistance, the current passing thru each shunt circuit would be the same and could be easily regulated by varying the number of battery cells used, or by introducing resistance in the main

circuit. If the different solutions offer varying counter electromotive forces and resistances the current flowing thru each shunt circuit must be regulated by a separate resistance. By using the proper switches and making the necessary connections the same set of measuring instruments may be used for the entire series of shunt circuits. Such an arrangement is presented in Fig. 38

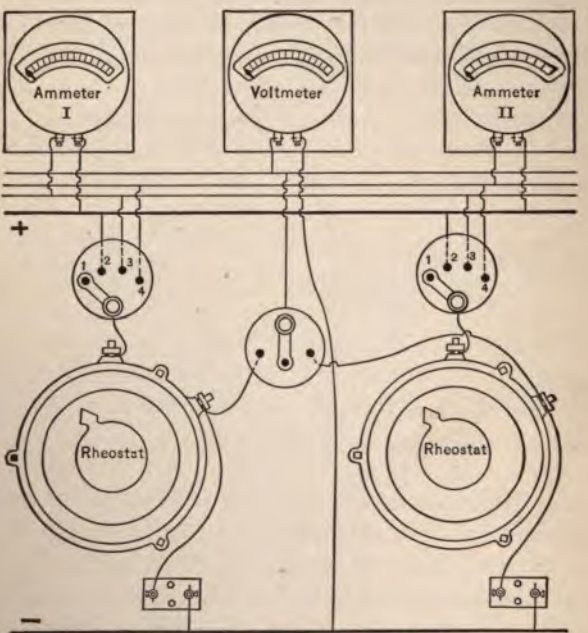

Fig. 38. — Plan of Wiring of Bench for Electrolytic Determinations

showing two out of any desired number of the shunt circuits, each of which is provided with a separate rheostat, and the connections by which either of two ammeters or a voltmeter may be thrown in or out of the circuit. One of these ammeters is used for the measurement of currents exceeding an entire ampere, the other

for fractions. The wires used for the connections are of copper and so large that their resistance may be disregarded.

The Use of Mechanical Stirring Devices.* It has already been shown that the efficiency of the current used is increased by improving the circulation of the solution. It is also easy to show that improving the circulation permits of the use of currents of much higher normal densities than would otherwise give satisfactory deposits under normal conditions. It becomes possible, therefore, to make precipitations with extreme rapidity by stirring the solution with a mechanical stirrer and using very strong currents, that is, from six to ten amperes. The stirrer used may be a small paddle wheel of glass rotated by a small electric motor or the anode or cathode may be made of such a form that they can be rotated by the same means.

* An excellent summary of the methods and results obtained with such devices will be found in A. Fisher's Electroanalytische Schnellmethoden.

CHAPTER XX

DETERMINATION OF CHLORINE IN SODIUM CHLORIDE

I. Facts Upon Which the Determination Is Based

Purity of Sodium Chloride. Sodium chloride which contains the theoretical percentage of chlorine can be obtained from dealers. Impure samples can be easily purified by preparing a nearly saturated solution, and passing a stream of hydrochloric acid gas into it until a sufficient amount of the salt precipitates, which is then separated on a Witt filter-plate and dried. It is not sufficiently hygroscopic to make accurate weighing difficult, but samples, which have stood in a moist atmosphere for some time may contain as much as one per cent of water.

Properties of Silver Chloride. When first precipitated silver chloride is very finely divided and is then retained on a filter with some difficulty; if, however, the solution is slightly acid, and if kept hot and stirred vigorously, or if allowed to stand for several hours the fine particles gradually coalesce, and, owing to their high specific gravity, rapidly settle to the bottom of the containing vessel. A solution of silver nitrate containing 24 gm. of the crystallized salt per liter forms a convenient reagent for the precipitation of chlorine; 1 cc. of such a solution should precipitate 0.005 gm. of chlorine.

The solubility of silver chloride is extremely small; it is increased by the presence of large concentrations of nitric and hydrochloric acid and the chlorides and nitrates of ammonium and the alkali metals. When digested with pure water it slowly changes into a colloidal form, but this change is prevented by the presence of a small amount of nitric acid or any other soluble electrolyte.

When freshly precipitated silver chloride is exposed to strong sunlight it darkens; this change is associated with the formation of a subchloride and the liberation of chlorine. Since the precipitate is not transparent the action is superficial only, and the percentage acted upon is small unless the mass of precipitate is continually broken up by stirring.

Pure silver chloride fuses at 460° without change of composition and produces a yellow viscous liquid, which forms a tough, horny mass when allowed to solidify. It begins to volatilize at about the same temperature, and appreciable amounts may be driven off if the heating is continued for some minutes.

Like most of the compounds of silver this precipitate is easily reduced to the metal by even weak reducing agents. The efficiency of organic matter as a reducing agent makes it necessary to use extreme care in igniting the precipitate when separated on a paper filter, and renders the use of an asbestos filter preferable.

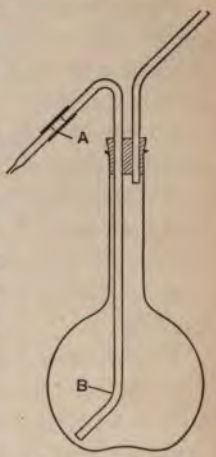

Fig. 39. — Wash Bottle

II. Preparation of a Wash Bottle

This determination requires the use of an efficient and convenient "wash bottle," similar to the one represented in Fig. 39. It should be provided with a flexible joint at *A* and two or more easily detachable nozzles, which can be used to produce streams of varying size. The delivery tube should be bent at *B* in order to permit of a more complete expulsion of the water when the flask is held in an inclined position.

III. Outline of Method of Procedure

Weighing Out the Sample. Place about 3 gm. of the salt in a porcelain or platinum crucible, cover and heat gradually with

a burner until the salt no longer decrepitates. Allow the crucible to cool somewhat, but while still warm pour the salt into a clean, well-stoppered sample tube; when the tube has assumed the temperature of the balance-room weigh accurately to a tenth of a milligram. Hold the tube over a clean 300 cc. beaker, remove the stopper and carefully pour into the beaker from 0.2 to 0.4 gm. (not more) of the sample, then replace the stopper and again weigh accurately.

Preparation of Solution and Precipitation. Dissolve the sample in 100 cc. of pure water, add 1 cc. of dilute nitric acid and then slowly and with constant stirring a slight excess of silver nitrate solution; 5 cc. of the reagent referred to above in excess of the amount theoretically required is sufficient. Next heat the solution gradually to the boiling point, and keep somewhat below this temperature, stirring continuously, until the precipitate coagulates and the supernatant liquid is clear; or allow the beaker to stand for several hours after heating to the boiling point. The beaker should be kept away from direct sunlight as much as possible.

Filtration and Ignition of Precipitate. Connect a clean Gooch crucible with a suction flask as shown in Fig. 29. Attach the flask to the suction pump and add to the crucible sufficient asbestos pulp to leave a compact layer about 2 mm. thick when drawn against the bottom of the crucible by means of the pump and place a thin Witt filter plate on top of the asbestos. Pass 100 cc. or more of water thru the filter till all loosely adhering fibers are rinsed from the outside of the crucible. Remove the crucible from the filter tube, place in a muffle and heat for about twenty minutes at a temperature of 200°. Cool in a desiccator and then weigh accurately.

Clean and rinse out the suction flask, connect the crucible with it as before, start the suction pump and decant the solution from the silver precipitate thru the crucible. Add to the precipitate in the beaker about 25 cc. of water, stir the mixture for a few

minutes, then allow it to settle and again decant thru the filter. Wash with three more 25 cc. portions of water, to each of which about one half cc. of dilute nitric acid has been added. Transfer the precipitate from the beaker to the filter by means of a stream of water from the wash bottle directed back of the precipitate. Finally loosen all particles of precipitate which adhere to the surface of the beaker by means of a rubber-tipped rod and rinse these also into the filter. Empty the filter flask and rinse with distilled water, again connect with the filter and pass 25 cc. of water acidified with nitric acid thru it and test the washings by adding a drop of dilute hydrochloric acid. If this test shows an appreciable turbidity continue washing with water containing a little nitric acid until another test shows that the silver salts have been removed. Finally wash with 10 cc. of pure water.

Place the crucible in a muffle, heat slowly to 200° and keep at that temperature for twenty minutes, then allow it to cool in a desiccator and weigh accurately. Again heat for ten minutes and reweigh and if necessary continue heating and weighing until two consecutive weighings do not differ by more than 0.3 mg. Calculate and report the percentage of chlorine found.

Further Details. This is an ideal precipitation process. The very slight solubility of the precipitate and the accuracy with which as much as two or even three grams of it can be transferred to a filter, dried and weighed, make it readily possible to reduce the error of the determination to a very small figure. The departure from the theoretical value need not exceed one-tenth of a per cent, and the entire determination can be made in a two-hour period after some experience has been acquired, if economy in the use of time is observed. The facts made use of in this determination can obviously be applied to the determination with equal accuracy of the silver in solutions of silver salts.

IV. Questions and Problems. Series 7

1. Calculate the concentrations, as defined on page 39, of the Ag and NO_3 ions in a solution containing 25 gm. of $AgNO_3$ per liter, assuming the salt at

this concentration is 70 per cent dissociated; also the concentrations of Pb and Cl ions in a solution containing .74 gm. of $PbCl_2$ in 135 cc., assuming the salt is 80 per cent dissociated.

2. Calculate the solubility products of AgCl, AgBr, and AgCNS from the data given on page 115, assuming that dissociation is complete.

3. Calculate the solubility in gm. per liter of AgCl in the solution obtained by dissolving .25 gm. of NaCl in 100 cc. of water and then adding 35.4 cc. of reagent $AgNO_3$ solution, assuming that all salts are completely dissociated. *Ans.* 4.1×10^{-6}.

4. If a dilute solution of $AgNO_3$ is slowly added to a solution which contains .2 gm. of NaCl and 0.005 gm. of KCNS, will AgCl or AgCNS separate first?

5. How would this determination be affected (a) by acidifying with dilute H_2SO_4 or $H(C_2H_3O_2)$ instead of HNO_3, (b) by dissolving in 150 instead of 100 cc. of water, (c) by using tap instead of distilled water, (d) if KCN or K_2S or $Na_2S_2O_3$ were present in the solution before the nitric acid was added?

6. If so much of the precipitate was reduced that one-fourth of the precipitate actually weighed consisted of Ag_2Cl, how large a departure from the correct result would appear in the report? *Ans.* 2.06 per cent.

7. If you were required to determine the percentage of iodine in sodium iodide by precipitating as silver iodide, would it be desirable to either increase or decrease the amount of sample used, as compared with the amount used in this determination? *Ans.* No.

8. How would you utilize the silver precipitates obtained in these determinations for the preparation of silver nitrate reagent?

CHAPTER XXI

DETERMINATION OF MAGNESIUM IN CRYSTALLIZED MAGNESIUM SULFATE ($MgSO_4 \cdot 7\,H_2O$)

I. Facts Upon Which the Determination Is Based

Outline of Method. The magnesium ion is precipitated by neutral or alkaline solutions of soluble phosphates, but the resulting precipitates may consist of mixtures of di- and tribasic phosphates, or of a number of double phosphates. Under certain conditions a pure precipitate of $Mg(NH_4)PO_4 \cdot 6\,H_2O$ can be obtained, and since this precipitate is converted into $Mg_2P_2O_7$ by ignition, magnesium is usually determined in this form.

Solubility of the Precipitate. The solubility of this precipitate is greater than that of most precipitates used; it cannot be accurately determined owing to a partial decomposition in pure water, which is represented by the expression

$$Mg(NH_4)PO_4 \cdot 6\,H_2O \rightarrow MgHPO_4 + (NH_4)HO + 5\,H_2O.$$

This reaction is reversed by the presence of moderate concentrations of ammonium hydroxide, and an excess of this reagent must be used in making the precipitation and in washing the precipitate, but a large excess should be avoided.

Conditions Necessary for Precipitation. A solution of $Na_2HPO_4 \cdot 12\,H_2O$ containing 74.50 gm. per liter, which is equivalent to 0.005 gm. of Mg per cc., is a convenient reagent to use for this precipitation. Experience shows that unless one and one-half times the theoretically required amount of reagent is present in the solution while the precipitate is separating, the results obtained are slightly low. It has also been shown that if the solution contains very large concentrations of NH_4 ions, high

results are obtained. This has been attributed to the formation of small amounts of $(NH_4)_4Mg(PO_4)_2$ which yields $Mg(PO_3)_2$ on ignition. The concentration of the NH_4 ions depends for the most part upon the concentration of the ammonium salts present, but in part upon the concentration of ammonium hydroxide.

Several chemists have formulated the exact conditions necessary to effect complete separation of magnesium in the desired form; the method devised by Gooch and Austin* will be used here. In this method the proper excess of sodium phosphate is first added to the neutral or slightly alkaline solution, which produces a precipitate assumed to contain small amounts of $Mg_3(PO_4)_2$. This precipitate is redissolved by adding a few drops of dilute hydrochloric acid and the magnesium reprecipitated by the *very gradual* addition of dilute ammonium hydroxide. Sufficient soluble phosphate is present during the second precipitation to insure complete precipitation and an undesirably large concentration of (NH_4) ions is avoided by this procedure.

The precipitate obtained should be coarsely crystalline; it shows some tendency for the formation of supersaturated solutions, but under ideal conditions complete separation should take place within a half hour. The separation is retarded by the presence of large concentrations of ammonium salts, and it is sometimes necessary to allow the mixture to stand for twelve hours or to stir vigorously for an hour.

Conditions Necessary for Ignition. A very high temperature must be used to convert $Mg(NH_4)PO_4$ into $Mg_2P_2O_7$, hence the precipitate should be ignited in a small crucible with a Méker or Chaddock burner, or over a blast lamp. At the temperature finally attained a slight sintering of the precipitate takes place, and if particles of unconsumed filter paper are still present they may be so surrounded as to prevent complete oxidation. Hence the temperature should be kept rather low until the combustible matter has been consumed. This difficulty can usually be avoided

* Zeit. für anorganische Chemie, **20**, 121 (1899).

by moistening the precipitate and filter with a few drops of a strong solution of ammonium nitrate before ignition.

Some chemists prefer to separate this precipitate on a Gooch crucible, but the large size of these crucibles increases the difficulty of bringing the precipitate to the proper temperature. Altho the precipitate is not readily reduced, it is not wise to ignite it in a platinum crucible as the latter becomes brittle and soon cracks if used repeatedly for this purpose; this is probably due to the formation of a small amount of a phosphide of platinum.

II. Outline of the Method of Procedure

Weighing Out and Precipitating the Sample. Place 3 to 4 gm. of the pure dry salt in a clean sample tube and weigh out about 1 gm. into a 200 cc. beaker. Dissolve the sample in about 50 cc. of water, add one and one-half times the theoretically required volume of sodium phosphate solution, and then add dilute hydrochloric acid drop by drop until the precipitate which usually separates redissolves. Dilute in a separate vessel 10 cc. of dilute ammonium hydroxide to 50 cc., and add this solution drop by drop with constant stirring until the solution when tested with a narrow piece of red litmus paper shows a slight alkaline reaction. Next add slowly 20 cc. of dilute ammonium hydroxide and allow the mixture to stand, stirring it occasionally, for one-half hour.

Filtration. Fold an 11 cm. ashless filter paper to accurately fit a funnel of slightly larger size and moisten with water. Decant the clear portion of the solution thru the filter, then transfer the precipitate to it by means of a stream from a wash bottle which contains a mixture of one volume of dilute ammonium hydroxide to four of water. Continue washing with this mixture until 20 cc. of the washings give no recognizable test for chlorine. Finally moisten the precipitate and filter with a few drops of a five per cent solution of ammonium nitrate.

Igniting and Weighing the Precipitate. Dry the filter and while waiting for it to dry ignite and weigh a small porcelain

crucible. Separate the precipitate as far as possible from the filter and complete the ignition as directed on page 132. The final ignition should be made with a cover on the crucible using the full heat of a Méker or Chaddock burner for at least twenty minutes, and repeating until consecutive weighings, which do not differ by more than 0.3 mg., are obtained. Difficulty is sometimes experienced in obtaining a perfectly white precipitate owing to incomplete combustion of small amounts of carbon. This is sometimes due to imperfect removal of soluble phosphates. It can often be corrected by adding a few drops of ammonium nitrate solution to the crucible and repeating the ignition.

Calculate and report the percentage of magnesium present.

III. Questions and Problems. Series 8

1. Why would you expect that the compound $Mg(NH_4)PO_4 \cdot 6\,H_2O$ might react with water? What reagents should reverse this reaction? Which of these could be used in washing the precipitate?

2. What reagents ought to reduce the solubility of $Mg(NH_4)PO_4 \cdot 6\,H_2O$? Which ones could be used for this purpose in the quantitative determination (a) of magnesium, (b) of phosphoric acid?

3. What factors would determine whether $Mg(NH_4)PO_4 \cdot 6\,H_2O$ or $Mg(NH_4)_4(PO_4)_2$ would separate in this determination?

4. What factors determine the completeness of the reaction which takes place when $Mg(NH_4)PO_4 \cdot 6\,H_2O$ is ignited? What would you expect to happen when (a) $MgNaPO_4$, (b) $Mg(NH_4)_4(PO_4)_2$ or (c) NaH_2PO_4 are heated? heated?

5. Calculate the chemical factors (see page 74) for converting $Mg_2P_2O_7$ into (a) MgO, (b) P_2O_5, (c) $MgSO_4 \cdot 7\,H_2O$, (d) $MgSO_4 \cdot Na_2SO_4 \cdot 4\,H_2O$.

6. What is the probable formula of a salt which is found to contain 5.97 per cent of Mg, 19.40 of K, 47.76 of SO_4 and 26.80 of water?

7. What other metallic ions may be present when this method is used for the determination of magnesium?

CHAPTER XXII

DETERMINATION OF IRON IN FERROUS AMMONIUM SULFATE BY THE USE OF THE ELECTRIC CURRENT

I. Facts Upon Which the Determination Is Based

Composition of Ferrous Ammonium Sulfate. This salt has the formula $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O$ and is readily obtained in a high degree of purity. As it slowly oxidizes and loses some of its water, even at 25°, it should be preserved in a stoppered bottle in a cool place. If these changes have taken place the crystals show a reddish color and lack their usual transparency.

Conditions Necessary for the Separation. The decomposition voltage of the ferrous ion is 0.34 volt higher than that of the hydrogen ion and the metal cannot be separated from solutions by an electric current unless the concentration of the hydrogen ion is small. It is not possible to separate the metal in a satisfactory form from solutions of simple ferrous salts, but good results are obtained if the solution also contains a large concentration of ammonium or potassium oxalate.

The solubility of ferrous oxalate is only 0.077 gm. per liter, and since double oxalates of ammonium and potassium are easily prepared, it is probable that most of the iron in such solutions is in the form of a complex ion. The composition of this ion is not definitely known, but its formation can be represented by

$$x\,FeC_2O_4 + y\,\overline{\overline{C_2O_4}} + 2\,y(\overset{+}{N}H_4) \rightarrow (FeC_2O_4)_x\overline{\overline{(C_2O_4)_y}} + 2\,y(\overset{+}{N}H_4).$$

It has been shown that for every atom of iron present in such solutions four molecules of potassium oxalate must be present to prevent the separation of a precipitate containing iron. Such precipitates are not easily dissolved by the addition of further

amounts of soluble oxalates, and in preparing the solution care must be taken to add the iron solution to a concentrated solution of the soluble oxalate. The voltage necessary for the separation of iron from such solutions is somewhat higher than that necessary to separate it from solutions of simpler composition.

Secondary Effects of the Electrolysis. The C_2O_4 ions present are slowly oxidized to CO_3 ions at the anode and since the temperature of the solution may rise to 60°, owing to the large amperages usually employed, much carbon dioxide is expelled. As NH_3 is not expelled to the same extent, the solution may acquire a sufficient degree of alkalinity to precipitate some of the iron; it then becomes necessary to add sufficient oxalic acid to dissolve the precipitate.

Properties of the Precipitate. The separated metal forms smooth coherent deposits even when deposited on foil electrodes, by the use of a current measuring as much as three amperes (normal density). It is not acted upon appreciably by the solution as usually prepared, but is rapidly dissolved by even small concentrations of mineral acids. It is easily oxidized, especially when moist, and must be rinsed with at least two changes of alcohol to displace the adhering water, dried at a temperature not in excess of 60°, and weighed without delay, if oxidation is to be avoided.

Effect of Additional Substances. Solutions containing ferric sulfate or chloride also form double oxalates, but since reduction to the ferrous condition precedes precipitation of the metal the time needed is greater. The presence of the NO_3 ion must be avoided, owing to its oxidizing power. The presence of all metals which stand below, or only slightly above iron in the electropotential series must be avoided.

II. Outline of Method of Procedure

Splitting a Watch Glass. The large amount of gas liberated during this electrolysis makes it necessary to cover the containing ·ssel; a watch glass which has been split into halves can be used

with advantage. To split the glass make a scratch on its convex surface with a steel or diamond glass-cutter, using a piece of cardboard for a straight edge, and then bring the glass along the scratched line into contact with a piece of fine nichrome wire which is heated to dull redness by means of an electric current. If the glass does not fall apart at once place a drop of cold water on the line heated by the wire.

Preparation of the Solution. Place about 5 gm. of the salt in a dry sample tube and weigh out about 1 gm. into a 100 cc. beaker. Add 25 cc. of water and stir until the salt dissolves. Weigh out approximately 6 gm. of crystallized ammonium oxalate into a 200 cc. beaker of narrow form, add 50 cc. of water, warm and stir till the salt dissolves. Add the iron solution to the oxalate solution, and rinse out the beaker with three 10 cc. portions of water. The resulting mixture should be perfectly clear and of a deep yellow color.

Electrolysis of the Solution. Ignite a clean platinum cathode of the Mansfeld or Winkler type in the flame of a burner, allow to cool without placing in a desiccator, and weigh accurately. Place the cathode in the iron solutions and an anode in the center of the cathode cylinder. Carry the beaker to the bench containing an installation similar to that represented in Fig. 38. Throw the ammeter and voltmeter switches opposite one of the vacant electrolytic stands to the point marked zero, and turn the arm of the adjustable rheostat well over to the left of the center as shown in the figure. Connect the cathode with the lower arm of the electrolytic stand and the anode with the upper arm, carefully adjusting both electrodes so that both extend to within a few mm. of the bottom of the beaker, but do not come into contact with one another.

Next note whether the needle of the ammeter (the one reading up to fifteen amperes) stands at zero, which means that the instrument is not being used on any of the other circuits, and if not at zero wait until out of use. As soon as the pointer of the instrument

stands at zero throw the ammeter switch to the point marked two and slowly turn the arm of the rheostat till the instrument shows that a current of one and one-half amperes is flowing thru the circuit; then throw the ammeter switch back to the point marked one. Next turn the voltmeter switch to the point nearest the circuit in use and after recording the reading of the needle return the switch to the central point.

Allow the current to run for 80 minutes if the Winkler cathode is used, or two hours if a Mansfeld cathode is used. At the end of this time the solution should be perfectly colorless and should show no traces of precipitate.

Washing and Weighing the Cathode. Fill a 200 cc. beaker with distilled water and place on the desk near the solution; raise the electrolytic stand without breaking the circuit or disconnecting the attached wires and plunge the electrodes without loss of time into the beaker of water. Add to the beaker containing the residual solution a few cc. of potassium ferrocyanide; if it gives a perceptible reaction for iron the determination should be repeated. If no iron is found in the solution, disconnect the cathode and rinse in the water of the beaker, then remove and bring into contact with a large piece of filter paper until most of the adhering water has been absorbed. Rinse the cathode in alcohol, using first the cylinder marked "for first washing," then the cylinder marked "for second washing," which should contain 98 per cent alcohol, and drain on a piece of filter paper. Dry in an air bath at a temperature of about 60°. Do not allow the alcohol on the cathode to catch fire; if it does so the precipitated iron will also burn, and the heat liberated will cause some of it to alloy with the platinum and spoil the electrode. Weigh the
de accurately and calculate the per cent of iron present.
ıe cathode in a beaker containing dilute sulfuric acid and
ɔ remain until absolutely all the deposited iron has been
ᵀ; this can be determined by noting whether hydrogen

III. Questions and Problems. Series 9

1. Explain why a large amount of gas is liberated at the cathode during the later stages of the deposition but not during the earlier.

2. On the basis of Faraday's law how long a time would be required to deposit all the iron present in 1 gm. of ferrous ammonium sulfate if a current of 0.5 ampere is used? Why is the calculation of no practical value?

3. Exactly why is the formation of a precipitate prevented by adding the iron solution to the oxalate solution?

4. If the ferrocyanide test used showed that iron was still present why not replace the electrodes in the solution and continue the electrolysis instead of discarding the determination?

5. If the decomposition voltage of a normal solution of the ferrous ion is +0.34 volt, what voltage would it be necessary to use to reduce the concentration of the ferrous ions to 0.00056 gm. in a volume of 100 cc.?

Ans. +0.456.

6. Why is the voltage necessary for the deposition of iron from a neutral solution of ferrous sulfate increased by the addition of ammonium oxalate?

7. Outline an electrolytic method for the determination of iron in a sample of iron wire and give all the reactions concerned.

8. How many storage battery cells, each of which is capable of furnishing 2.2 volts, would be necessary to give the voltage required for ten simultaneous determinations, assuming that the fall of potential per solution is 0.5 volt, that the resistance of each solution and connections is 0.5 ohm and that a current of at least one ampere is maintained (a) when the solutions are in series, (b) when they are in parallel? Would it be advisable to decide upon the number of cells from the voltage calculated?

9. Show by means of a simple diagram the course of the current during electrolysis when the ammeter switch (a) is at the point 2, (b) is at the point 4 of Fig. 38, (c) when the voltmeter switch is at such a position that the voltage is registered.

CHAPTER XXIII

DETERMINATION OF SULFUR IN IRON PYRITES

I. Facts Upon Which the Determination Is Based

Composition of Pyrites. This mineral is represented by the formula FeS_2, but it is frequently associated with the sulfides of other metals, especially copper, zinc, arsenic and lead, with the sulfates of calcium and barium, and almost invariably with silica and various insoluble silicates. It is assumed that the sample used for this determination contains at least 35 per cent of sulfur, only small amounts of copper, zinc and arsenic, and neither barium nor lead. It is assumed further that the sample has been crushed and passed thru a sixty-mesh sieve, carefully mixed and dried.

Methods of Oxidizing Sulfides. Two methods are in general use for the oxidation of naturally-occurring sulfides; in one the mineral is treated with a strong mineral acid and a strong oxidizing agent, such as potassium chlorate, nitric acid or bromine; in the other it is fused with a mixture of sodium carbonate and either sodium peroxide or potassium nitrate. The presence of NO_3 ions in the solution from which barium sulfate is to be precipitated must be avoided, owing, as shown on page 135, to the extent to which nitrates are occluded. Since, however, the NO_3, ClO_3 and Br ions can be easily expelled by evaporating the solution with a large excess of hydrochloric acid, and since no sulfuric acid is expelled if this evaporation is made on a steam bath, there is no objection to the method of oxidation first named. The presence of the large amounts of sodium and potassium salts necessarily introduced in oxidizing by the fusion process also results in errors from occlusion, and since these salts cannot be removed from the

solution by any satisfactory process this method of oxidation is to be avoided.

Most samples of pyrites can be completely and rapidly oxidized by means of a mixture of three volumes of concentrated nitric and one of concentrated hydrochloric acid. In some instances, especially where the temperature of the mixture is allowed to rise too high, and the decomposition of the sample takes place too rapidly, small amounts of free sulfur may separate; this can usually be oxidized by the addition of a few drops of liquid bromine, whose oxidizing properties are stronger than those of nitric acid. Treatment of the sample with this mixture and the subsequent evaporation with hydrochloric acid insures complete oxidation of the iron and arsenic, and renders all constituents soluble except silica and the insoluble silicates.

Separation of the Iron Before Precipitation of Barium Sulfate. The filtrate from the insoluble matter will contain large amounts of ferric chloride, also the chlorides of the other metals present. If barium sulfate is precipitated from such a solution it will contain occluded ferric sulfate and, as shown on page 134, this will lead to very low results.

If the iron is precipitated by the addition of ammonium hydroxide, appreciable amounts of ammonium salts are added to the solution, and as ammonium sulfate is both occluded by the precipitate and expelled during ignition, a rather large error may result unless the amount of acid present in the solution before precipitation is reduced to a minimum.

The precipitate obtained by the addition of ammonium hydroxide to a solution containing ferric sulfate may contain appreciable amounts of basic sulfates, unless a relatively large excess of precipitant is used and the mixture heated for some time. Even when no basic sulfates have been formed, it is difficult to wash out the last traces of soluble sulfates from the precipitate, and it is not safe to discard the latter until it has been proved to be free from these compounds. The washed precipitate can be dissolved

in a very small amount of warm dilute hydrochloric acid, the iron again separated and the sulfur precipitated in the resulting filtrate. Under the proper conditions the weight of barium sulfate obtained from the second filtrate should not exceed 10 mg., and is often inappreciable. Where extreme accuracy is not essential the method may be abbreviated somewhat by precipitating the small amount of barium sulfate in the hydrochloric acid solution of the precipitate, without removing the iron.

Properties of Barium Sulfate. The solubility of barium sulfate amounts to 2.2 mg. per liter; it is increased by small concentrations of nitric or hydrochloric acid; it is decreased by small concentrations of sulfuric acid or salts which yield SO_4 ions, but the salt is decidedly soluble in concentrated sulfuric acid. It has a density of 4.49 gm., and when precipitated under the proper conditions settles rapidly. As much as 2 gm. of the precipitate can be easily and rapidly filtered and washed on an 11 cm. filter.

The barium sulfate precipitate is usually classed as pulverulent, but its properties are affected to a large extent by the conditions of precipitation. That produced by the addition of a salt of barium to a cold concentrated solution of a soluble sulfate is often so finely divided that it cannot be retained on the filters usually employed. Altho long-continued digestion increases the size of the particles of which such a precipitate is composed, it is preferable to avoid the formation of such precipitates by causing it to separate from a hot solution whose concentration does not exceed 3 gm. of SO_4 per liter. The presence of a small amount of acid makes the precipitate more compact, causes it to settle more rapidly, and reduces its tendency to creep.

The conditions which result in the formation of a precipitate of the most desirable physical properties also result in a slight tendency for supersaturation. Under the conditions which are recommended later the precipitate should be allowed to stand for at least one hour before filtration; increasing the amount of acid increases the time necessary for complete separation.

The precipitate produced by the addition of a salt of barium to a slightly alkaline, or even to a neutral solution of a soluble sulfate may contain, in addition to barium sulfate, small amounts of basic sulfates, and, also, as the result of the absorption of carbon dioxide from air, of barium carbonate. The presence of a slight concentration of hydrogen ions prevents the formation of either of these compounds. If, however, the concentration of the hydrogen ions is not kept very small, low results are obtained, owing to the fact that under these conditions appreciable amounts of an acid sulfate of barium is occluded. The maximum concentration of hydrogen ions should not exceed 0.02 gm. per liter.

Conditions Necessary for Ignition. Pure barium sulfate is not decomposed appreciably by heating in dry air up to a temperature of 1400°. If heated in the presence of carbon, carbon monoxide, or other reducing agents it is partly reduced to the sulfide even at a temperature of 600°; the presence of moisture also seems to favor this reduction. If the precipitate is ignited with the filter paper without previous drying appreciable amounts of barium sulfide may form, unless the temperature is kept very low until all of the water and volatile organic matter has been driven off. If some of the precipitate has been reduced it can be changed back into the sulfate by moistening with dilute sulfuric acid, evaporating to dryness and igniting.

II. Outline of Method of Procedure

Oxidation of the Sulfur. Weigh out 0.5 gm. of the sample into a 150 cc. beaker, cover with a watch glass, add 10 cc. of a mixture of three volumes of concentrated nitric and one of concentrated hydrochloric acid and allow to stand for ten minutes. If brown fumes are not evolved at the expiration of this time warm the beaker gently until the mixture begins to react; if the action becomes too violent, restrain it by placing the beaker in a dish of cold water. When brown fumes are no longer given off and when the residue contains no particles of a brassy-yellow color it may be

assumed that the decomposition of the sample is complete. If decomposed too rapidly, yellow or greenish-yellow particles, which consist for the most part of free sulfur, will float in or on the solution; the oxidation should then be completed by adding one or two drops of liquid bromine (not bromine water) and allowing to stand on the steam bath for a few minutes.

Displacement of Nitric Acid. Remove the cover from the beaker, rinse off the former with a little water and evaporate the solution to dryness on the steam bath, then add 10 cc. of dilute hydrochloric acid and evaporate to dryness as before. Moisten the residue with 1 or 2 cc. of dilute hydrochloric acid, add 50 cc. of water and digest until all soluble salts have been brought into solution, noting especially that the ferric sulfate present in the residue often dissolves very slowly.

Separation of Gangue and Iron. Filter through a 7 cm. filter into a 300 cc. beaker and wash with at least 50 cc. of cold water. Dilute the filtrate to 150 cc., heat nearly to boiling and add ammonium hydroxide until the resulting mixture smells of ammonia and all of the iron seems to be precipitated. Keep the mixture near the boiling point for about five minutes, then allow the solution to stand till most of the precipitate has settled. Decant off the clear portion of the solution thru an 11 cm. filter, receiving the filtrate into a 500 cc. beaker, then transfer the precipitate to the filter and wash with hot water "churning up" the precipitate frequently with a stream from the wash bottle, and using about 200 cc. of wash water in all; this forms filtrate No. 1.

Set aside the beaker containing the filtrate and place the beaker in which the iron was precipitated under the funnel. Transfer as much of the precipitate as can be readily picked up by means of a stirring rod to the bottom of the empty beaker, taking care to avoid rupturing the filter; at least three-fourths of the precipitate can be easily transferred by this means in a few minutes. Add sufficient warm dilute hydrochloric acid, drop by drop, to the precipitate

still remaining on the filter, to completely dissolve it, using not more than 10 cc. of the reagent, preferably less. Wash the filter with cold water long enough to remove the ferric chloride and make it colorless, finally warm the mixture in the beaker until a perfectly clear yellow solution is obtained. Dilute the solution to 150 cc., reprecipitate the iron as before and again filter and wash, receiving the filtrate (filtrate No. 2) in a 500 cc. beaker.

Precipitation of Barium Sulfate. Add to both filtrates (No. 1 and 2) a drop of methyl orange indicator, then dilute hydrochloric acid until the solutions are slightly red and then three drops of acid in excess. Heat filtrate No. 1 to boiling and add with constant stirring 30 cc. of barium chloride solution, 1 cc. of which is equivalent to 0.01 gm. of sulfur, also heated nearly to boiling. Heat filtrate No. 2 in like manner and add 10 cc. of barium chloride solution. Allow both precipitates to stand for at least one hour, then filter on separate filters and wash thoroughly with hot water and dry.

Igniting and Weighing Precipitate. Burn the filter containing the precipitate from filtrate No. 2 in a porcelain or platinum crucible; separate the precipitate obtained from filtrate No. 1 from its filter and burn the latter, in the same crucible. Finally add the main precipitate to the crucible and ignite for at least ten minutes over a good flame, allow to cool and weigh accurately. Calculate the percentage of sulfur present in the original sample.

III. Additional Notes on the Determination

This determination is of much industrial importance and has been made the subject of many investigations.* Duplicate determinations by the method here outlined need not differ by more than 0.2 per cent, and give very nearly the true percentage of

* See Hinze and Webber, Zeit. für analytische Chemie, **45,** 31 (1906); Allen and Johnston, Jour. of Industrial and Eng. Chem., **2,** 196 (1910); Allen and Bishop, Eighth Int. Congress of Applied Chemistry, Vol. I, page 33 (1913).

sulfur present. An entire determination can be completed within three hours in addition to the time the precipitate is allowed to stand before filtering.

IV. Questions and Problems. Series 10

1. A lump of ore weighs 500 gm. and consists of 20 per cent quartz (sp. gr. 2.8) and 80 per cent pyrite (sp. gr. 5). If the sample is crushed, mixed and quartered twice, and again crushed and mixed, what is the maximum permissible size of particle for the three crushings in order that the portions removed at the two successive quarterings and the 0.5 gm. portion used for the analysis shall represent the correct composition of the sample with an error not exceeding 0.1 per cent? (For method of calculation see page 27.)

Ans. 4.7, 2.96 and .75 mm.

2. What advantages are there in keeping the filtrate from the two iron precipitates separate rather than uniting them?

3. How would you proceed in order to determine the amount of barium chloride occluded by the precipitate of barium sulfate found?

4. What is the percentage error of a determination of sulfur in which the 0.874 gm. of precipitate found and assumed to be pure $BaSO_4$ actually contains 0.02 gm. of Na if the Na is occluded as suggested on page 139?

5. If the ash of the filter paper used weighed 0.0002 gm., how large a departure from the correct percentage would result from failure to correct for it, assuming that 0.5 gm. of sample is used and that it contained 40 per cent of sulfur?

6. Write the reactions which probably take place when pure pyrite is treated with aqua regia. What is the action of (a) pure bromine, (b) of bromine water?

CHAPTER XXIV

SEPARATION OF CALCIUM FROM MAGNESIUM AND PARTIAL ANALYSIS OF LIMESTONE

I. Facts Upon Which the Analysis Is Based

Composition of Limestone. This rock invariably contains, in addition to calcium and magnesium carbonates, small amounts of the carbonates and oxides of iron, manganese and alumina, and more or less quartz, clay and other silicates. The minerals pyrite, graphite, apatite and gypsum are frequently associated with limestone.

Proximate Method of Analysis. This analysis forms one of the problems frequently presented to the analyst since limestone is an essential raw material in many branches of chemical technology. The complete analysis takes much time and labor, and for many technical uses is unnecessary; hence in many factories it is customary to make a more rapid "proximate analysis," in which certain groups of constituents, which are present in small amounts only, are separated and reported as a whole, rather than being resolved into their ultimate elements.

If the sample is treated with nitric or hydrochloric acid the quartz, graphite and most of the silicates remain undissolved. If the amount of insoluble matter left is very small it is frequently ignited, which effects combustion of the graphite, weighed, and reported as "gangue" or "insoluble matter." If the amount present is larger it is usually considered necessary to treat the sample as an insoluble silicate (see Chapter XXVII), or to treat the gangue matter which has been separated as an insoluble silicate.

The iron, aluminum and phosphoric acid are almost invariably separated from the other bases present by the use of ammonium hydroxide. The resulting precipitate can be resolved into its ultimate constituents by methods discussed in other chapters of this book; they are more frequently weighed together and reported as mixed oxides. The small amount of manganese which is sometimes present can be separated with approximate accuracy from the filtrate by the addition of bromine, which causes this element to separate as the hydrated dioxide.

The loss which results from ignition represents still a third group of constituents of which carbon dioxide is by far the most important; this determination is sometimes substituted for the more accurate estimation of this constituent.

After eliminating all of the elements named only calcium and magnesium remain. As the percentages of these elements often have an important practical significance they are usually determined with considerable care and accuracy.

Sources of Error in the Determination of Gangue. This determination furnishes an illustration of a solution process dependent upon the chemical action of a reagent (see Chapter XXVIII). Since certain silicates such as clay are but slowly acted upon by the acids used the results obtained depend to some extent upon the fineness of the sample, the length of time it is treated and the composition of the acid used; there is no generally accepted standard method of procedure. Sufficient nitric acid should be present to dissolve any pyrite, and to effect complete oxidation of the iron. After decomposition has been effected the solution should be evaporated to complete dryness to dehydrate and render insoluble the silicic acid formed (see Chapter XXVII).

Sources of Error in the Determination of Iron and Alumina. Ferric hydroxide and aluminum hydroxide form bulky precipitates, which are extremely difficult to filter and wash. When separated by the addition of ammonium hydroxide, from a solution which also contains calcium and magnesium, the resulting precipitate

invariably contains these elements also, even tho a large amount of ammonium chloride was present. This is due in part to the difficulty of washing the precipitate and to occlusion; it may also have resulted from the absorption of carbon dioxide by the reagent before use or by the mixture after precipitation and formation of insoluble calcium carbonate.

Ammonium hydroxide acts upon glass, especially the ordinary soft glass, appreciably, and solutions which have stood in bottles for some time invariably contain a scale-like precipitate which is largely composed of silica; it can be removed by filtration, but the filtered solution may still contain small amounts of soluble silica, some of which may separate when the reagent is used. Hence when results of the greatest accuracy are demanded this precipitation must be made in vessels of resistant glass or still better of platinum, and the ammonium hydroxide used must be freshly distilled. In commercial work the only precaution usually taken is to filter the reagent, and to reduce its concentration and the time it is in contact with the containing vessel to a minimum.

The hydroxides of iron and aluminum are converted into the corresponding oxides at a temperature of about 600° and much higher temperatures can be used without danger of further changes. Ferric oxide is easily reduced to lower oxides by organic matter at this temperature.

Properties of Calcium and Magnesium Oxalates. Crystalline calcium oxalate ($CaC_2O_4 \cdot 2\,H_2O$) dissolves in water to the extent of 5.6 mg. per liter. If precipitated from an alkaline solution it is finely divided and bulky, but if precipitated from an acid solution it is coarsely crystalline. It occludes magnesium, and to a less extent sodium, potassium and ammonium salts, probably as the result of its tendency to form double salts of these metals. The amount of occlusion is reduced by precipitating from a solution containing a slight excess of free acid; under such conditions, however, the precipitation is incomplete and altho about 80 per cent can be separated from a solution which is distinctly acid, the

remainder must be separated from a solution which is distinctly alkaline. For these reasons it is decidedly preferable to separate most of the precipitate by the addition of a solution of oxalic acid to the neutral or barely acid calcium-containing solution, and the balance by neutralizing the resulting mixture. A reagent which contains 45 gm. of crystallized oxalic acid ($C_2H_2O_4 \cdot 2\,H_2O$) per liter (1 cc. of which is equivalent to 0.02 gm. of CaO) is a convenient one to employ.

Magnesium oxalate ($MgC_2O_4 \cdot 2\,H_2O$) is soluble in water to the extent of 300 mg. per liter, but shows a remarkable tendency to form supersaturated solutions, so that the apparent solubility may rise to three hundred times the normal value. Supersaturated solutions of this kind deposit a large part of the excess of dissolved salt rapidly but much of it is retained in solution even after long standing.

Calcium is not completely precipitated from solutions containing large amounts of magnesium salts unless an excess of C_2O_4 ions are present. If sufficient C_2O_4 ions are present to combine with both the calcium and magnesium present the precipitation is complete; excessive concentrations of C_2O_4 ions must be avoided to prevent the solution from becoming supersaturated with respect to magnesium oxalate.

The properties of these oxalates which are enumerated above make it necessary to adopt and adhere to certain definite conditions in separating calcium from magnesium. The weight of oxalic acid used, as compared with the weights of calcium and magnesium present, and the total volume from which the precipitate is made to separate are of especial importance. The directions which are given below are especially designed for the analysis of limestone;* they also apply to samples in which the proportion of magnesium to calcium is much greater than that found in limestone provided the amount used is sufficient to furnish a total weight of 0.4 gm. of the two oxides.

* Jour. of Amer. Chem. Soc., **31**, 918 (1909).

Theory of the Method Used. The occlusion of magnesium by calcium oxalate has been made the subject of many investigations, but it was first shown by Richards * that the error from this source could be greatly reduced by the presence of large concentrations of NH_4 ions or of small concentrations of hydrogen ions. This seems to be due to the fact that a large concentration of NH_4 ions must increase that of the complex magnesium-ammonium ion and reduce that of the simple magnesium ion, and, therefore, that of the undissociated magnesium oxalate. Similarly, since the hydrogen ion represses the ionization of oxalic acid, it reduces the concentration of the C_2O_4 ion, and, therefore, that of the undissociated magnesium oxalate. As the amount of occlusion depends upon the concentration of the undissociated magnesium oxalate either reagent should reduce the error from this source.

Weighing the Calcium Precipitate. Altho crystallized calcium oxalate loses most of its water at 200° it is difficult to expel all of it without causing some of the precipitate to decompose into calcium carbonate and carbon monoxide. It can be completely changed into the carbonate by heating for a long time at 400° or into the oxide by heating to 850°. As the oxide rapidly absorbs both water and carbon dioxide it must be weighed in a covered crucible as rapidly as possible.

The Separation of Magnesium. The filtrate from the calcium has a large volume and contains a large amount of ammonium chloride and some ammonium oxalate. These conditions make it necessary to modify somewhat the method used in Chapter XXI. The large concentration of the NH_4 ion greatly retards the separation of the precipitate and gives it an abnormal composition. Hence it becomes necessary to concentrate the solution, to make a preliminary precipitation in which the precipitate is allowed to stand for ten hours, to separate and redissolve this precipitate and to make a final precipitation as in the analysis of magnesium sulfate.

* Proc. Am. Acad. of Arts and Sciences, **36**, 375 (1901).

II. Outline of Method of Procedure

Separation of the Gangue. Weigh out about .7 gm. of the finely-ground sample into a 200 cc. beaker, cover with a watch glass and gradually introduce 20 cc. of dilute hydrochloric and 5 of dilute nitric acid. When violent action ceases, heat the beaker on a steam bath long enough to insure complete decomposition, that is, until no more gases are liberated. Then remove the watch glass, rinsing off the under surface with a stream from a wash bottle, and evaporate to complete dryness. To the residue add 10 cc. of dilute hydrochloric acid and digest five minutes, or until the basic salts or oxides which may have formed have been entirely dissolved. Add 20 cc. of water, filter thru a 7 cc. filter, wash four times with 10 cc. portions of water and drain. Place the still moist filter in a weighed crucible and heat cautiously over a wire gauze until the water has been expelled and the paper consumed; finally ignite over a direct flame for about ten minutes, then cool and weigh accurately. Calculate and report the per cent of gangue present.

Separation of Iron and Aluminum. Warm the filtrate from the gangue and add to it slowly and with constant stirring recently filtered ammonium hydroxide until the solution smells distinctly of the reagent. Place the beaker on the sand bath and keep at a temperature slightly below the boiling point for about ten minutes, or until the odor while still easily recognizable is not unpleasantly strong. This should cause the separation of a small amount of a precipitate whose color may vary from red-brown to white; if it is dark brown or black it indicates that manganese is present it, probably because the concentration of ammonium chloride he solution was too small. Filter on a 7 or 9 cm. filter and with water containing about 20 gm. of ammonium chloride which prevents the aluminum hydroxide from forming . Redissolve the precipitate in a small amount of hydrochloric acid and dilute to 50 cc.; reprecipitate,

filter and wash as before, receiving the filtrate in the beaker containing the first filtrate, and acidify with hydrochloric acid. Treat the precipitate finally separated like the gangue matter, calculate and report the total percentage present.

Determination of Manganese. Concentrate the solution to 75 cc. or less, neutralize with ammonium hydroxide and add 5 cc. of the reagent in excess, then add a few drops of liquid bromine or 30 cc. of bromine water and heat slowly to the boiling point. If a precipitate forms filter at once on a 7 cm. filter, wash with hot water and ignite at a good red heat, without separating from the filter, till the weight is constant. Calculate and report the per cent of MnO from the weight of Mn_3O_4 found.

Determination of Calcium. Acidify the filtrate from the manganese and boil till the liberated bromine is expelled and the solution colorless, then dilute to 300 cc., add a drop of methyl orange indicator and sufficient ammonium hydroxide to change the color from pink to salmon yellow. Heat to boiling and add slowly and with constant stirring 22 cc. of oxalic acid solution, set aside for ten minutes, then add very slowly, that is, over an interval of at least five minutes, 3 cc. of ammonium hydroxide, which has been diluted to 30 cc. with water. If this does not make the solution distinctly alkaline add a further quantity of the reagent in the same manner. After the precipitate has stood for an hour, filter thru a 9 cm. filter and wash with water until free from chlorine. Place the filter in a porcelain or platinum crucible, which has been weighed with its cover, and destroy the filter as in the determination of gangue; finally heat the crucible over a Méker or Chaddock burner for at least twenty minutes. Cool in a desiccator for thirty minutes, and weigh as rapidly as possible. Continue igniting and weighing until two consecutive weighings do not differ by more than 0.3 mg. Calculate and report the percentage of calcium oxide thus obtained.

Determination of Magnesium. Acidify the filtrate from the calcium with dilute hydrochloric acid, evaporate to a volume of

200 cc. and cool. Add 25 cc. of the sodium phosphate reagent, then slowly introduce 25 cc. of dilute ammonium hydroxide, which should impart a strong odor of ammonia to the solution, and finally set aside for at least ten hours. Decant off the solution thru a 9 cm. filter and discard the filtrate; place the beaker containing the main part of the precipitate under the filter and pour thru it the smallest possible amount of hydrochloric acid needed to dissolve the precipitate on the filter and in the beaker (some 5 cc. of the reagent diluted to 25 cc. should suffice); then wash the filter free of soluble compounds.

Next add to the solution in the beaker, which should have a volume of about 50 cc., 5 cc. of sodium phosphate solution and then sufficient ammonium hydroxide to make it distinctly alkaline and give an excess of 3 cc. Stir the mixture occasionally during an interval of twenty minutes, then filter on a 9 cm. filter and wash with dilute ammonium hydroxide as in the analysis of magnesium sulfate.

Separate the precipitate and weigh as in the analysis of magnesium sulfate. Calculate the percentage of magnesium oxide present.

Determination of Hygroscopic Water. Weigh out 0.8 gm. of the sample in a 10 cc. platinum or porcelain crucible, which is provided with a cover. Place in a drying oven and heat to a temperature of 105° for an hour, and weigh accurately. Calculate the per cent of hygroscopic water from the loss in weight thus found.

Determination of Loss on Ignition. Place the crucible containing the residue from the previous determination on a wire triangle and heat over a Méker or Chaddock burner until the ght is constant, using all of the precautions used in the ignition calcium oxalate precipitate. Calculate the percentage loss rt as loss on ignition.

calculate all the percentages thus far obtained to show n of the water-free sample.

III. Questions and Problems. Series 11.

1. Are there any objections to precipitating iron (a) with KOH instead of $(NH_4)OH$, (b) in the ferrous instead of the ferric condition, (c) from a solution of the sulfate or nitrate rather than the chloride?

2. What experiments might be made for the purpose of showing that $Al(HO)_3$ forms a hydrosol? What reagents might be used to prevent the formation of a hydrosol in the quantitative determination of aluminum?

3. Express all of the important reactions which take place when $MnCl_2$, $(NH_4)Cl$, $(NH_4)HO$ and Br are added to water in the order named. What takes place when the mixture is made acid with HCl?

4. What reaction takes place when MnO_2 is ignited? What is the simplest form of the equilibrium expression representing this reaction?

5. If the sample of limestone used for this analysis contained small amounts of strontium or barium carbonates, in what manner would it have affected the determinations here outlined?

6. Under what conditions would it be possible to dehydrate calcium oxalate without changing some of it into the carbonate?

7. How can you determine from the curves of Fig. 16 whether heat is absorbed or liberated, when you determine the loss or ignition?

8. Indicate the equilibria which are of importance when the occlusion of magnesium by calcium is reduced by the presence of HCl.

9. Suppose a sample of limestone contained, in addition to 5 per cent of insoluble silicates, only $CaCO_3$ and $MgCO_3$, and suppose further that the loss on ignition amounted to 45 per cent, what percentages of calcium and magnesium are present?

CHAPTER XXV

ANALYSIS OF ALLOYS CONTAINING TIN AND LEAD

I. Facts Upon Which the Method Is Based

Composition of Samples. These alloys contain from 20 to 70 per cent of tin and are used as solders; their market value depends mainly upon the percentage of tin present which is the more expensive metal. Traces of other metals, especially copper, zinc, iron and antimony are sometimes present. As the alloy is usually cast and sold in the form of long, thin bars, which are fairly homogeneous, an average sample is easily obtained by cutting thin shavings from the length of the bar.

Decomposition of the Alloy. Alloys which contain large percentages of lead are but slowly attacked by either sulfuric or hydrochloric acids, largely owing to the slight solubility of the sulfate and chloride of lead; dilute nitric acid acts more energetically, and forms lead nitrate and metastannic acid; concentrated nitric acid acts more slowly, owing to the slight solubility of lead nitrate in strong nitric acid. If dissolved in concentrated nitric acid, or if dissolved in dilute nitric and evaporated to dryness the tin present is completely changed into metastannic acid. This treatment also favors the separation of metastannic acid in a form which permits of easy and rapid filtration.

Properties of Metastannic Acid. The solubility of this compound in water and dilute nitric acid is known to have a very small value only; its solubility in dilute hydrochloric is greater, and in dilute sulfuric it is quite large. It possesses a remarkable tendency to occlude metals, especially iron, lead, copper, zinc and manganese, probably owing to the formation of insoluble salts of

metastannic acid. The amount of lead occluded when tin-lead alloys are decomposed is less when the nitric acid used is very strong, but even under the most favorable circumstances the error from this source is too large to neglect when the precipitate amounts to more than a few milligrams.

Freshly precipitated metastannic acid is readily dissolved by moderately strong solutions of ammonium sulfide with the formation of ammonium sulfostannate; if precipitates which contain any of the occluded metals named above are treated with this reagent these metals separate as insoluble sulfides. If nitric acid is added to a solution of ammonium sulfostannate, a mixture of sulfur and stannic sulfide separates, but when the concentration of the acid is large, or if the mixture is heated, the stannic sulfide slowly forms metastannic acid. The resulting mixture is difficult to filter, owing to the fineness of the particles. If a solution of ammonium sulfostannate is evaporated to complete dryness and the residue treated, first with dilute and then with concentrated nitric acid, the sulfur which separates can be fused into a single globule, which can be readily removed; the metastannic acid can then be separated by filtration and ignited without being reconverted into stannic sulfide.

Metastannic acid is slowly but completely converted into stannic oxide by heating to 500°. It is easily reduced by organic matter even at lower temperatures; the oxide is not appreciably hygroscopic.

Properties of Lead Sulfate. This is a pulverulent precipitate; it has a specific gravity of 6.23, settles rapidly and as much as 1 gm. of it can be readily filtered and washed. Its solubility in pure water is about 44 mg. per liter. This is reduced by the addition of sulfuric acid up to the point at which the mixture contains about 10 per cent by volume of the concentrated acid; beyond this concentration the solubility begins to increase. It is also increased by the presence of even small concentrations of hydrochloric and nitric acids, and in the quantitative separation

of lead sulfate these acids must be expelled by evaporating with an excess of sulfuric acid. Its solubility is greatly decreased by the presence of even small concentrations of alcohol.

Pure lead sulfate can be heated without danger of decomposition up to 400°. As it is very easily reduced by heating in the presence of organic matter, and as the metal is decidedly volatile, extreme care must be taken in igniting the precipitate.

II. Outline of the Method of Analysis

Preparation and Decomposition of the Sample. Prepare the sample by cutting about 2 gm. of thin shavings from a bar of the alloy by means of a dull knife, and place in a clean, dry sample tube. Weigh out 0.5 gm. of the sample into a 200 cc. beaker, cover with a watch glass, add 10 cc. of concentrated nitric acid and then from 5 to 10 cc. of water, using the larger amount if the sample is but slowly attacked. Heat the beaker on the steam bath long enough to disintegrate the sample, that is, until all hard lumps have disappeared and a fine white powder only remains; then remove the cover and evaporate to a volume of 3 cc.

Separation and Purification of Metastannic Acid. Add to the beaker 5 cc. of concentrated nitric acid and 30 cc. of water, heat nearly to boiling and digest for ten minutes; while waiting prepare a glass filter tube with a thin layer of finely shredded asbestos and connect with a clean filter flask. Pass the liquid in the beaker thru the filter, refiltering if necessary, to obtain a perfectly clear filtrate, and wash three times with 10 cc. portions of water. Transfer the filtrate to a clean 250 cc. beaker, wash out the flask with at least four portions of water and place on a steam or sand bath to evaporate.

Invert the filter tube over the bottom of a clean 200 cc. beaker, push the filter plate and asbestos into the beaker by means of a glass rod or wire passed thru the stem of the tube, and rinse any adhering fibers of asbestos into the beaker by a few cubic centimeters of water. Next remove the filter plate and rinse this also,

then add 10 cc. of a strong solution of ammonium sulfide made by saturating concentrated ammonium hydroxide with hydrogen sulfide. Disintegrate the asbestos by means of a glass rod, warm the mixture slightly until all white particles have been dissolved and only a fine black residue of lead sulfide remains. Prepare a second asbestos filter, moisten with a few drops of ammonium sulfide solution, filter the solution of sulfostannate of tin thru it, wash four times with water containing a few drops of ammonium sulfide and twice with pure water. Transfer the solution in the filter flask to a clean 400 cc. beaker, wash four times with water, place on a steam or sand bath and evaporate to complete dryness. Warm about 5 cc. of dilute hydrochloric acid in a small beaker and pour over the filter containing the lead precipitate, which should cause the filter to become pure white, then wash with hot water and transfer the solution to the beaker containing the main part of the lead.

Determination of Lead. Add to the beaker containing the lead solution 5 cc. of concentrated sulfuric acid, which should be introduced cautiously if the solution is warm; evaporate on the sand bath till white fumes of sulfur trioxide are given off, watching the mixture very carefully during the later stages of the process as it may bump and sputter. When cool, add 45 cc. of water and set aside for at least one-half hour. While waiting for the completion of these operations, prepare a Gooch crucible with a good layer of asbestos; ignite and weigh accurately. Filter the lead sulfate precipitate thru the crucible thus prepared, wash four times with 10 cc. portions of 20 per cent alcohol, dry at about 300° and weigh. Calculate the percentage of lead present.

Determination of Tin. Add to the beaker containing the dry residue resulting from the evaporation of the sulfostannate solution 10 cc. of dilute nitric acid, cover at once with a watch glass and warm gently till further action ceases; next add 10 cc. of concentrated nitric acid and again warm for a few minutes. Rinse off the sides of the beaker and the watch-glass cover and set the latter aside, then evaporate the mixture to nearly complete

dryness. The large amount of sulfur which separates in a free condition should finally fuse to form a clear yellow liquid, all of which should be collected into a single large globule before it solidifies.

Add to the residue 5 cc. of dilute nitric acid and 50 cc. of water, digest for ten minutes, then filter on a 9 cm. filter and wash free from acid for if much acid is left in contact with the precipitate the filter will become brittle and will crumble on drying. Separate the filter as completely as possible from the precipitate and set the latter aside on a watch glass. Remove the globule of sulfur from the precipitate, which may contain very small amounts of tin, and burn in the crucible. Next, burn the filter in the crucible and finally add the main precipitate and ignite over a wire triangle with a Méker burner or blast lamp, for twenty minutes. If the resulting precipitate is decidedly gray moisten with a few drops of concentrated nitric acid, evaporate off the acid, and again ignite. Calculate the percentage of tin from the weight of stannic oxide found.

III. Questions and Problems. Series 12

1. Show how the action of nitric acid on metallic tin might give rise to either stannous nitrate, stannic nitrate or metastannic acid.

2. Indicate the reaction of ammonium sulfide on the tin-lead precipitate.

3. What determines the volume of sulfuric acid which should be added to the solution which contains the lead before evaporating to dryness?

4. What factors make it easy to completely displace the nitric acid from this solution?

5. What effect would you expect the presence of large amounts of Cu, Fe, Zn or Sb to have on the analysis?

6. What weight of $PbSO_4$ should be dissolved by 100 cc. of a solution made by diluting 2 cc. of concentrated sulfuric acid to 100 cc., assuming that the normal solubility is reduced according to the solubility product principle? Why does the method of calculation used involve large errors in this case?

CHAPTER XXVI

ANALYSIS OF BRASS

I. Facts Upon Which the Method Is Based

Composition of Sample. The essential constituents of this alloy are copper and zinc; it sometimes contains small percentages of tin and lead and traces of iron, antimony and other metals, which represent impurities in the metals of which the alloy was made. A homogeneous sample can usually be obtained by drilling holes in the ingot or bar, or by placing in a turning lathe and cutting thin shavings from it. If the sample has been already made into drillings or shavings it should be carefully examined for particles of wood or iron with which it is sometimes contaminated.

Conditions for Separation of Tin and Lead. The alloy is readily dissolved in either strong or dilute nitric acid and essentially the same conditions as were used for the determination of tin and lead in solder can be used here. The amount of tin present is usually so small that it is not ordinarily necessary to purify it for occluded metals.

Conditions for Separation of Copper from Zinc. The decomposition voltage of copper is 0.33 volt lower and that of zinc 0.71 volt higher than that of hydrogen, hence the two metals are easily separated in the presence of sufficient free acid by the constant current method. But little difficulty is experienced in obtaining good deposits of copper in the presence of NO_3 ions, and currents of 0.5 ampere normal density can be used if a gauze electrode is employed. If a foil electrode is used it is scarcely safe to use currents greater than 0.05 ampere normal density. The precipitated metal is rapidly dissolved by even dilute nitric acid and is slowly oxidized even at a temperature of 100°.

Conditions for Determination of Zinc as Phosphate. When a soluble phosphate is added to a neutral solution of a zinc salt which also contains a large concentration of ammonium salts, a flocculent precipitate separates; if this precipitate is digested for a short time it is slowly converted into a crystalline precipitate having the formula $Zn(NH_4)PO_4 \cdot H_2O$. This precipitate is appreciably soluble in solutions containing even small concentrations of either hydrogen or hydroxyl ions; hence the solution must be made as nearly neutral as possible. It is also essential that the solution should contain a large concentration of NH_4 ions and a large excess of PO_4 ions. The solubility of the precipitate in either hot or cold water is but slight, and it is easily washed free from soluble salts.

The crystalline zinc ammonium phosphate readily loses all of its water if dried at 105°; it can also be converted into the pyrophosphate on direct ignition, but, as with the corresponding transformation of the magnesium compound, it undergoes partial reduction and fusion at a bright red heat; hence it is preferable to separate on a Gooch crucible rather than on a paper filter.

II. Outline of the Method of Procedure

Determination of Tin. Weigh out 3 gm. of the sample into a 100 cc. beaker, add 25 cc. of dilute nitric acid and cover with a watch glass. Action should begin to take place almost at once and complete solution should be effected within a few minutes; if not, warm the beaker slightly by placing on the steam bath. If the action at any time becomes too violent it should be restrained by placing the beaker in a vessel of cold water. When the alloy is completely dissolved remove and rinse off the watch-glass cover, again place on the steam bath, and allow to evaporate to complete dryness.

Add to the residue 5 cc. of dilute nitric acid and 25 cc. of wate and allow to digest till the basic salts of copper, which usuall

separate as a voluminous blue-white precipitate, are brought into solution. If a fine white residue of metastannic acid still remains, filter on a small filter, wash till free from acid, dry, ignite and weigh. Calculate the percentage of tin from the stannic oxide thus found.

Determination of Lead. Add to the filtrate from the tin 7 cc. of concentrated sulfuric acid and evaporate until the nitric acid has been expelled and dense white fumes of sulfur trioxide are given off. This will not occur until the total volume is less than 7 cc. and the temperature of the solution has risen to about 250°. During the evaporation of the solution the sulfates of lead, copper and zinc separate, and unless the precipitate is kept in constant motion, and unless the temperature is kept below 100°, violent bumping and spiriting is certain to take place. For this reason it is best to evaporate on the steam bath until most of the water is driven off, and to complete the evaporation on a sand bath or sheet of asbestos while stirring the mixture vigorously and continuously.

When the dish is cold add 50 cc. of water, stir until the soluble sulfates have been dissolved and only sulfate of lead remains, then set aside for half an hour. While waiting for these operations, prepare and weigh accurately a Gooch crucible, connect the crucible with a clean filter flask, filter off the precipitate on it, wash four times with a mixture of equal parts of water and dilute sulfuric acid, and twice with 20 per cent alcohol. Heat the crucible slowly to a temperature of about 250°, cool and weigh accurately. Calculate the percentage of lead present from the weight of lead sulfate thus found.

Division of the Solution. Transfer the solution containing the copper and zinc to a 250 cc. graduated flask, dilute till the lowest part of the meniscus corresponds to the line on the neck of the flask, stopper with a tightly fitting cork and mix thoroughly by alternately inverting and rotating the flask. Measure out three 50 cc. portions of the solution as follows: pour out about 20 cc. of the brass solution in a small beaker and use this to rinse

out a clean but not necessarily dry 50 cc. pipet, discarding the solution after using it. Next, suck up a further quantity of the liquid into the pipet until it rises above the mark on the stem of the pipet and allow to drain back into the flask until the lowest point on the curve of the meniscus corresponds to the mark on the stem of the pipet; remove the pipet from the flask and allow the solution to flow into a clean 150 cc. beaker and to drain for two minutes, but do not wash out with water.

Determination of Copper by Electrolysis. To one of the solutions which has been separated, add sufficient ammonium hydroxide to make it slightly alkaline, then 2 cc. of concentrated nitric acid. Ignite and weigh accurately a clean platinum cathode, place in the solution and add water enough to cover the electrode. Introduce a spiral anode and connect both with the terminals of a storage battery. Change the resistance in the circuit by means of a rheostat until a current of 0.5 ampere if a gauze electrode is used, or of 0.05 ampere if a foil electrode is used, passes thru the solution. Allow the electrolysis to proceed for fifteen minutes after the solution has become colorless, if a gauze electrode has been used, or for three hours after the solution has become colorless, if a foil electrode has been used. The entire time necessary should be about ninety minutes and twelve hours, respectively.

Place a small beaker containing sufficient water to cover the cathode on the bench near the solution being electrolyzed, raise the stand supporting the electrodes and, without disconnecting the attached wires, plunge the electrodes into the beaker of pure water. Allow the current to pass for a few minutes, rinse the electrodes by rotating the beaker, then disconnect the cathode, remove from the water, allow to drain and absorb as much of the water as possible by bringing into contact with a piece of filter paper. Rinse the cathode in at least two changes of 95 per cent alcohol, absorb the excess of alcohol by means of filter paper and dry for a few minutes at a temperature of about 50°, which can

be done by holding over a sand bath for a few minutes; then weigh accurately, and calculate the percentage of copper present.

Determination of Zinc. Evaporate the aqueous washings from the cathode to a small bulk and transfer both the washings and the residual solution to a 300 cc. beaker; add ammonium hydroxide until the solution is neutral to litmus paper, heat to boiling, add 80 cc. of sodium phosphate solution and again neutralize the solution very carefully with either dilute ammonium hydroxide or hydrochloric acid, as may be found necessary.

Heat the solution almost to the boiling point and keep at that temperature for fifteen minutes, that is, until the flocculent precipitate which separates at first becomes crystalline. Set the mixture aside for half an hour and while waiting, prepare and weigh a Gooch crucible. Filter off the precipitate, wash free from soluble salts with pure water, dry, ignite gently at first and then at a bright redness, cool and weigh accurately. Calculate the percentage of zinc present from the weight of zinc pyrophosphate found.

III. Questions and Problems. Series 13

1. Would it be desirable to vary the volume of sulfuric acid added before evaporation if the amount of sample used was varied, or if the relative amounts of copper and zinc in the sample varied?

2. Calculate by means of Faraday's law the time theoretically required to precipitate 0.3 gm. of copper with a current of 0.5 ampere, and show why the calculation has but little significance in this determination.

3. Explain how the addition of sodium hydrogen phosphate to the neutral solution containing zinc and ammonium salts may increase the concentration of the hydrogen ions present.

4. Explain the advantage of starting with 3 gm. of sample and using a fractional part of the solution for the determination of copper and zinc.

5. What other metals would separate with the copper under the conditions used in this determination?

6. If small amounts of copper were left unprecipitated, would it be recognized later?

CHAPTER XXVII

DETERMINATION OF SILICA IN A HORNBLENDE

I. Facts Upon Which the Determination Is Based

Methods of Decomposition. Silicates of the insoluble class, such as the hornblendes and the great majority of the naturally-occurring silicates, must be decomposed by means of hydrofluoric acid, or changed into silicates of the soluble class by fusion with certain fluxes. If the hydrofluoric acid method is employed the decomposition must be carried out in vessels of platinum, and since the silicon present forms volatile silicon fluoride, it cannot be determined unless the apparatus has a form which makes it possible to absorb all of the liberated gas in an appropriate reagent. Such an apparatus would be too expensive for general use.

The transformation into silicates of the soluble class can be effected by fusion with any strongly basic reagent, such as the hydroxides, oxides or carbonates of metals of the sodium and calcium group. Such fusions must necessarily be carried out in vessels free from silicon; a platinum crucible is to be preferred, but one of silver or nickel is sometimes used. A mixture of four parts sodium and five parts potassium carbonates, which melts at 685° is most frequently used; it does not attack platinum appreciably. As these reagents usually contain appreciable percentages of silica it becomes necessary to determine the percentage present and apply a correction to the final result. When a finely-powdered sample of hornblende is heated to a temperature of about 600° with this mixture, silicates and aluminates of sodium and potassium are produced and the corresponding amount of carbon dioxide liberated.

The Dehydration of Silicic Acid. When a soluble silicate is treated with an excess of hydrochloric acid, free silicic acid and the chlorides of all the metals present are formed. If the acid used is dilute and the temperature is kept low the silicic acid may remain in solution, but if these conditions are not complied with most of it separates as a gelatinous colloid, which is extremely difficult to filter. When the mixture is evaporated to dryness the silicic acid gradually loses water and assumes a fine, powdery form.

Experience shows that complete conversion of the silicic acid into an insoluble form is not easily effected. Some chemists dry the residue from evaporation at a temperature of 120° for a half hour or more, but this results in the formation of compounds of iron and alumina which are very difficult to dissolve; others dry at 105° or evaporate to complete dryness on the water bath several times. Two evaporations with an intermediate filtration of the dehydrated silicic acid are more effective than two successive evaporations, but even when this method is adopted small amounts of silica may be left in the solution. In dissolving the soluble salts from the residue left after evaporation either cold water or hot dilute acid should be used; if hot water alone is employed the iron and aluminum present may form insoluble basic salts. Even when the mixture is evaporated on the water bath only, the silica obtained may contain small amounts of iron and aluminum, but the error resulting from this is largely counterbalanced by the error from incomplete dehydration. Where the highest degree of accuracy is demanded it becomes necessary to volatilize the silica in the precipitate by treating it with hydrofluoric and sulfuric acids in a platinum crucible, and determining the impurities, representing iron and aluminum oxides, remaining; also, to separate the silica, which has remained in the solution, but is subsequently precipitated with the iron and alumina. These refinements are not usually considered necessary in commercial work.

The ignition of a silica precipitate requires extreme care owing

to its fine, powdery nature. If the paper filter used is heated too rapidly, and especially if it catches fire and burns at the mouth of the crucible, appreciable amounts of the precipitate may be carried off by the air currents formed. There is no danger of reducing or otherwise changing the composition of the precipitate, but long-continued ignition at the highest temperature readily attainable with a burner is necessary to completely convert the precipitate into the dioxide.

II. Outline of Method of Procedure

Selection and Preparation of the Sample. Carefully select from the roughly crushed sample about 3 gm. of the pure mineral. Place half gram portions at a time in a clean agate mortar and grind each portion until the resulting powder tends to form a compact thin layer on the side of the mortar and no longer feels gritty when rubbed between the fingers. Place a perfectly clean 100-mesh sieve over a piece of glazed paper, brush the powdered mineral into the sieve and tap it until all of the fine powder has passed thru it. Return the powder left on the sieve to the mortar and continue grinding and sifting until all of it has passed thru the sieve. Finally transfer the powdered mineral into a clean, dry, well-stoppered weighing tube.

Fusion. Weigh out in a platinum crucible of at least 10 cc. capacity about 4 gm. of fusion mixture. Weigh the tube containing the silicate and pour from it into the crucible about 0.7 gm. of the sample and again weigh accurately. Thoroughly mix the silicate with the fusion mixture by the use of a platinum spatula or a stirring rod, which has a carefully rounded end, then brush ·m the latter any of the adhering mixture and tap the crucible he mixture is well settled.

e the crucible on a triangle and heat it with a low flame five minutes, then gradually increase the temperature ıss begins to fuse and keep at this point until carbon ıger evolved. The crucible should be kept covered

to avoid loss from spattering and the temperature must be carefully controlled or the mixture may boil over. The entire fusion should require from twenty minutes to half an hour and should finally yield a quiescent mass of perfectly sintered but only partially fused material.

Decomposition. Remove the crucible from the triangle by means of a pair of forceps while still hot, and by carefully tipping and rotating the latter cause the contents to solidify as a layer around its inner surface. When cold place the crucible on its side in the bottom of a five-inch casserole, add 50 cc. of water, warm and stir until the fused mass is disintegrated and falls out of the crucible, then remove the crucible from the dish with the aid of a glass rod and wash both inner and outer surfaces thoroughly. Cover the dish with a watch glass and gradually introduce 20 cc. of hydrochloric acid. The dish should now contain only gelatinous silicic acid and a clear yellow solution. If sandy or gritty particles are present the decomposition is probably incomplete and a second sample must be fused. Sometimes the precipitated silica has a reddish color owing to the presence of difficultly soluble iron compounds, which usually dissolve on digestion.

Separation of Silica. Place the dish on the steam bath and evaporate to complete dryness, that is, till powdery dry. The evaporation may be made more rapidly by heating on a sand bath, or over a gauze placed some distance above the flame of the burner if the precipitate is kept in constant motion with a stirring rod. Moisten the residue with about 10 cc. of concentrated hydrochloric acid and then add 1 cc. of nitric acid and 50 cc. of water, and digest on the steam bath until all basic salts have been decomposed and white silicic acid only remains.

Filter thru an 11 cm. filter and transfer the precipitate to the filter, then wash twice with 10 cc. portions of cold water. Next transfer the filtrate and washings which may still contain small amounts of silicic acid to the casserole previously used, evaporate the mixture to complete dryness on the steam bath and keep the

dry residue on the bath one half hour longer. While the solution in the dish is evaporating continue to wash the silica precipitate until the washings are shown to be free from chlorine, receiving the washings in a clean 300 cc. beaker.

Treat the residue from the second evaporation with 20 cc. of dilute hydrochloric acid and digest until all basic salts have been decomposed, add 50 cc. of water and then filter thru a fresh 9 cm. filter, receiving the filtrate in the beaker containing the washings from the first silica precipitate. Next rub the entire inner surface of the dish with a rubber-tipped rod until the adhering precipitate has been loosened, and rinse into the filter; finally wash the latter until free from soluble salts. If this treatment has failed to remove all of the precipitate from the dish, moisten with a little dilute ammonium hydroxide and again rub with a rubber-tipped rod.

Place the two still moist filters in a weighed crucible and heat cautiously over a wire gauze until combustible gases are no longer given off; if these gases are permitted to take fire a sufficiently strong draft may be created to cause a mechanical loss of some of the precipitate, which is very light. Place the crucible over a wire triangle and gradually increase the temperature until the paper is entirely consumed; finally ignite over a blast lamp, or Méker burner for at least twenty minutes and weigh. Repeat the ignition till the weighings are practically constant.

Determination of Silica in Reagents. Weigh out 10 gm. of the fusion mixture used into a casserole, cover with a watch glass and cautiously introduce sufficient dilute hydrochloric acid to decompose it. Evaporate to complete dryness and separate the silica as in the analysis. Calculate the weight of silica in the weight of fusion mixture used in the analysis and subtract from the weight of precipitate found. Report the corrected per cent of silica

SECTION IV

SOLUTION AND EXTRACTION PROCESSES

CHAPTER XXVIII

GENERAL FEATURES OF SOLUTION AND EXTRACTION PROCESSES

Solution Processes Which Depend Upon the Physical Action of the Solvent. These processes depend upon the differential action of liquids on mixtures composed of two or more solids. The simplest possible example is one in which the mixture consists of two distinct solid phases, each phase representing a single component, one of which is much more soluble in some particular liquid than the other. If the difference in solubility is sufficiently large, and if the mixture is so finely divided that every particle of the more soluble constituent is exposed to the action of the solvent, treatment of the mixture with a sufficient amount of the solvent at once yields a liquid phase which contains all of the more soluble component, and a residual solid phase composed of the less soluble component. The action concerned is the converse of that of precipitation processes, but the rate at which equilibrium is attained when a liquid acts upon a solid is slower than when a precipitate is formed in a liquid, and altho the theory of the two classes of methods is essentially the same the methods by which they are carried out are decidedly different.

The ideal method of making such a separation would be to use only sufficient solvent to bring into solution all of the more soluble component, but such a method of procedure would not be practicable owing to the slowness with which solution of the last particles of the more soluble constituent is effected, and the adherence of

some of the liquid to the solid phase, which makes it necessary to wash the residue with further quantities of the solvent. The general theory of the method actually used in carrying out such processes is similar to that elaborated in Chapter XVII for the washing of precipitates. The comparative rates at which the two components pass into solution, the effect of one component upon the solubility of the other, the size of the particles of which the mixture is composed, and the relative amounts of the two components, all affect the accuracy and efficiency of such processes. An ideally perfected method for making a separation of this kind would prescribe the weight of the mixture to be used, the composition and amount of the solvent to be used for each treatment, the number of treatments, and the length of time allowed for each treatment. These details are best determined empirically, that is, by quantitative experiments with mixtures of known composition; in many of the processes largely used these details have only been determined very roughly.

In discussing the theory of this class of methods it is assumed that the two components of the mixture exist as distinct and separate solid phases. Some doubt should always be entertained as to whether the method can be successfully applied to the separation of a mixture of isomorphous substances which has separated from a solution, or has resulted from the solidification of a molten magma; that is, wherever the presence of solid solutions is possible. A solvent which readily dissolves one of the two components of a solid solution will often, especially where the less soluble component is present in relatively small amounts, readily disintegrate and decompose such a mixture, but not in all cases.

This class of methods is of especial use in the separation of those
ıts all of whose compounds are largely soluble in aqueous
and which, therefore, cannot be separated by the use
ation methods. In using them it is often necessary
'he substance to be separated into those particular

compounds which possess the necessary differences in solubility in some particular solvent.

Solution Processes which Depend Upon the Chemical Action of the Solvent. Processes in which the action of the solvent is chemical as well as physical are also extensively used. In all such cases two sets of equilibria must be considered. The equilibrium resulting from the contact of solvent and one of the solids must result in the formation of a single liquid phase, that is, must involve a change from heterogeneous to homogeneous equilibrium; that resulting from contact of the solvent with the other solid must involve maintenance of the original condition.

As in the case of processes in which the action of the solvent is purely physical the formation of solid solutions often makes it impossible to effect separations which could otherwise be easily made. The chemical as well as the physical properties of solid solutions are specific properties of the mixture, and vary with the comparative amounts of the two components actually present. Thus, altho metallic silver is readily changed into a solution of silver nitrate by treatment with a dilute solution of nitric acid, it is not possible to separate silver from gold in an alloy which contains more than 30 per cent of gold because the two metals form a continuous series of solid solutions.

Extraction Processes. Further difficulties are encountered in applying this class of methods to the analysis of certain classes of materials such as plant and animal tissues. In such substances the soluble constituent may be diffused thru or surrounded by cell walls, which act as semi-permeable membranes and prevent diffusion of the solvent. The difficulty can be overcome to some extent by mechanical disintegration and crushing of the sample, but even where the sample is reduced to a very fine powder it is often necessary to treat it with the solvent for many hours. To successfully carry out such a separation by supporting the mixture on a filter and washing with the solvent is impracticable, as it necessitates the use of very large amounts of the solvent, which is

often an expensive reagent, and demands a large amount of time and care from the analyst. It is then necessary to "extract" the substance in an apparatus of especial construction, which is known as an "extraction apparatus."

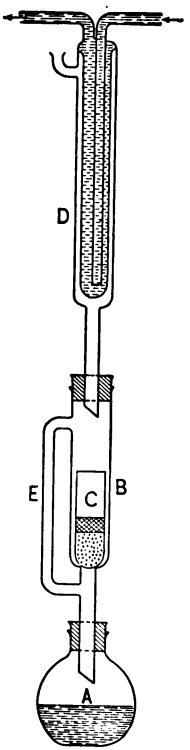

Fig. 40. — Continuous Extraction Apparatus

Extraction methods are of especial importance in the analysis of mixtures containing organic compounds, for, owing to the low temperatures employed in carrying on the process, and the slight activity of the solvents which are most frequently used, the probability of decomposing these compounds is reduced to a minimum. They are universally used in the analysis of substances of animal or vegetable origin, of all classes of explosives, and of asphalt paving materials.

Apparatus for Continuous Extraction. The conditions necessary for the rapid and complete extraction of any solid substance are most readily and effectively maintained by boiling the solvent in a small flask attached to an inverted condenser so arranged that the condensed solvent is made to fall into, and drip thru, a filter containing the substance to be extracted. An apparatus of this kind is represented in Fig. 40. It consists of a wide-mouthed flask *A* of about 125 cc. capacity, which contains the boiling solvent; an extraction tube *B*, which supports the "extraction shell" *C* containing the sample; and the condenser *D*. The vapor of the boiling solvent passes thru the side tube *E* into the condenser, and after condensation falls into the extraction shell, where it comes into contact with the sample, passes thru the shell, and falls back into the flask. Fresh portions of the pure warm solvent are thus continuously brought into con- and made to pass thru the shell and its contents, and

gradually wash out those constituents which are soluble. As these are usually much less volatile than the solvents used they accumulate in the flask in the form of a solution, whose concentration increases as the process of extraction progresses.

A more compact, and in some respects more desirable, apparatus is the one devised by Wiley, which is represented in Fig. 41. The substance to be extracted is here placed in a Gooch crucible *C*, which is suspended from the very efficient metallic condenser *B*; both crucible and condenser are contained in the tube *A*, which holds the boiling solvent. Both figures represent forms of extraction apparatus in which the distilled and condensed solvent is made to leach the sample continuously and are therefore designated as "continuous."

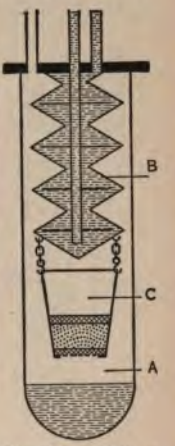

Fig. 41.—Wiley Extraction Apparatus

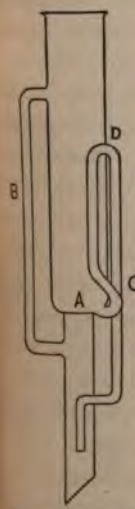

Fig. 42.—Soxhlet Extraction Tube

Apparatus for Intermittent Extraction. Another type of apparatus, of which there are also many forms, acts intermittently. It is represented by the Soxhlet apparatus shown in Fig. 42 and differs from the apparatus already described in the form of the extraction tube. This is closed at the point *A*, but is provided with a side tube *B* thru which the vaporized solvent passes into the condenser, and a siphon tube *C* thru which the solution, which accumulates in the extraction tube, runs back into the flask as soon as it reaches the level *D*. The action of this type of apparatus is distinguished by the fact that a large volume of the solvent remains in contact with the sample for a relatively long time; since, however, there is little circulation, that portion of the solvent in immediate contact with the sample soon attains a fairly large degree of concentra-

tion with respect to the soluble compound, which delays further solution. By using the method of reasoning already employed in discussing the theory of washing precipitates it is easy to show that the continuous type of apparatus should be more efficient than the intermittent, and a comparison of the efficiency of the two types under similar conditions confirms the accuracy of this conclusion; furthermore, the amount of solvent required to operate the continuous type of apparatus is much less than that required for the intermittent.

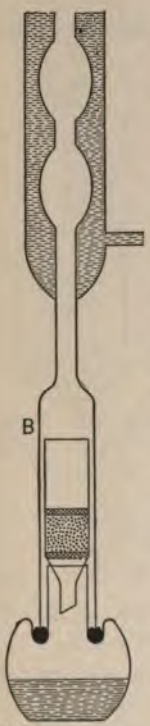

Fig. 43. — Knorr Extraction Apparatus

Construction of Joints to Apparatus. The solvents which are most extensively used are alcohol, ethyl ether, petroleum spirit, chloroform, carbon disulphide and carbon tetrachloride. All of these are extremely volatile, and all except chloroform are extremely inflammable. It is essential, therefore, that all joints of the apparatus should be tight, and that the condensation of the vaporized solvent should be as perfect as possible. Rubber dissolves in all of the solvents named except alcohol to some extent, and such media as wax or paraffin, which are sometimes used to remedy the deficiencies of cork stoppers, are also dissolved by these solvents appreciably. It is desirable, therefore, to use an apparatus, like the Wiley apparatus already described, which has no joints, or one which is made entirely of glass; if the latter alternative is adopted the ground-glass joints which become necessary must be very carefully made, and they are both expensive and easily broken.

Still another alternative involves the use of an apparatus, such as the Knorr apparatus represented in Fig. 43 or the Ames apparatus represented in Fig. 44, in which the only joint which is [illegible] to the action of the solvent is provided with a "mercury

In both forms the flask in which the solvent is made to is provided with a groove into which the tube *B* fits loosely, intervening space being filled with sufficient mercury to prethe escape of any of the vaporized solvent. here these more elaborate and therefore expensive types of apparatus are not able, recourse must be had to simpler s, in which the joints are made by means rk stoppers. These can usually be made ve tight joints if corks of good quality large size are chosen, boiled in water n hour, and while still hot and plastic d into the opening to be closed, and then ed to dry in this position; they should be l to fit the necessary connections when nd cold.

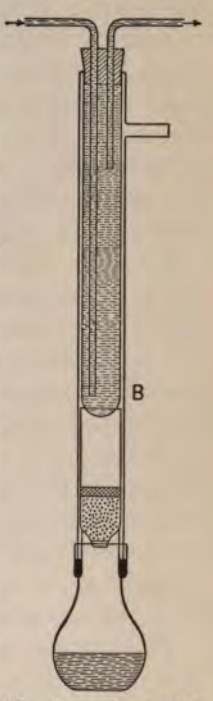

Fig. 44.—Ames Extraction Apparatus

ethods of Heating the Apparatus During action. Since the rate at which the le constituent is leached out depends upon ate at which the solvent circulates thru xtraction shell, it is desirable to heat the nt by means of a device which causes it il vigorously and steadily, that is, withlanger of boiling over. Direct heating of lask with a flame is always to be avoided, it is hard to regulate the rate of boiland if the flask cracks or if the joints of pparatus are not tight the flame may set fire to the escaping nt. The use of a water bath is more satisfactory but has disadvantages. An electric hot plate or an air bath heated current passing thru resistance wires or incandescent lamps be preferred to all other devices, since the danger from fire is ced to a minimum and any desired temperature can be maind by the use of proper resistances in the circuit.

Determination of the Separated Constituent. The weight of the constituent dissolved from the sample can be determined from the difference between the weight of the sample and that of the solid residue left, or if the substance extracted is not appreciably volatile, the solvent can be distilled off from the solution and the desired weight determined directly. Where the former method is used difficulties may arise from the hygroscopic character of the residue or of the extraction shell used. The alternative method of procedure is always to be preferred unless the dissolved constituent is so volatile that appreciable amounts of it are carried over with the solvent during the distillation.

Multiple Extraction Apparatus. Altho the actual labor involved in making a determination by an extraction method is small, it is often necessary to extract a sample for several hours, and where a large number of such determinations have to be made it becomes almost imperative to operate a number of such apparatus simultaneously. Many forms of multiple extraction apparatus in which a series of extraction units are supported on a common frame, and supplied with a common source of heat and condenser water, are in use. An apparatus* consisting of five such units is represented in Fig. 45; this apparatus is also provided with a common device for the distillation and condensation of the solvent after the extraction has been completed.

The heating device here used consists of five electrically-heated iron plates supported on a wooden base, but separated from it by a sheet of asbestos. The edge of each plate is surrounded by a strip of mica, which prevents the plate from short-circuiting the resistance wire by which it is heated, but does not prevent the transfer of heat to it. A nichrome wire 0.01 mm. in diameter passes thru a series of cleats fastened to the bed and makes three complete turns around, and in close contact with, the edge of each of five plates; this wire is connected directly with the ter-

* For details concerning the construction of this apparatus will be found in Jour. of Ind. and Eng. Chem., 4, 302 (1912).

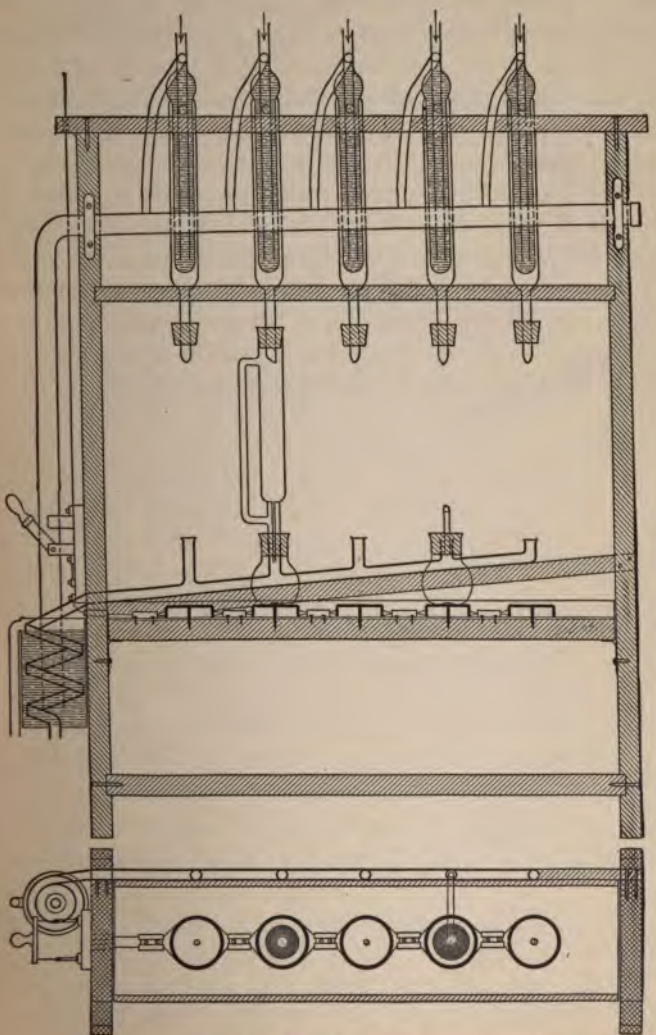

Fig. 45. — Plan of a Multiple Extraction Apparatus

minals of a 110-volt alternating current by means of a switch. The wire offers a resistance of 75 ohms and consumes 1.5 amperes.

The condenser used during distillation consists of a worm of block tin tubing supported in and surrounded by a cylindrical copper vessel thru which the waste water from the other series of condensers can be made to flow. One end of the worm passes thru the bottom of the copper vessel, the other is prolonged and supported in a position slightly inclined to the horizontal on a strip of wood fastened to the back of the frame of the apparatus. The prolonged end is provided with five vertical branches placed at points opposite to the centers of the five heating plates. Connection can be easily established between any of the flasks resting on one of the plates and the lateral opposite it by means of a glass tube.

CHAPTER XXIX

DETERMINATION OF POTASSIUM IN COMMERCIAL POTASSIUM SULFATE

I. Facts Upon Which the Method Is Based

Composition of Samples. This salt is largely used as a fertilizer and its commercial value is proportional to the percentage of potassium, usually reported as K_2O, which it contains. In addition to sulfate of potassium it contains sulfates and chlorides of sodium and magnesium.

Choice of Method. With the exception of a complex nitrite, which has the formula $KNa_2Co(NO_2)_6$, the compounds of potassium are too soluble in water to make it possible to determine this element by a precipitation process. The two methods, which have been most largely used up to the present time, involve conversion of the element into the perchlorate ($KClO_4$) or chloroplatinate (K_2PtCl_6) in a solid form, and elimination of all of the other salts present in the mixture thus obtained, by treating it with certain solvents, that is, by methods which are essentially solution processes. Of the three methods suggested the chloroplatinate method is to be preferred, especially where the amount of potassium present is small, on account of the large molecular weight of the compound finally separated and weighed, and also because the details of the method have been carefully worked out. Altho the reagent used is very expensive the platinum can be easily recovered after use and reconverted into a further quantity of reagent.

Formation of Potassium Chloroplatinate. Solutions containing mixtures of potassium and sodium chlorides are completely converted into K_2PtCl_6 and $Na_2PtCl_6{\cdot}6H_2O$ respectively, by evaporating almost to dryness with the theoretically required

amount of chloroplatinic acid. The potassium salt separates in well-formed octahedra belonging to the regular system; the sodium salt in plates belonging to the triclinic system. The two compounds do not form double compounds nor solid solutions with each other, nor with the chlorides of sodium, potassium, platinum or magnesium. The sulfate of potassium is readily changed into the chloroplatinate by the same treatment, but the sulfate of sodium is not so readily changed into the corresponding sodium compound. The reagent used for this purpose should be of known strength and of high concentration if economy in its use and in the time needed for the evaporation is to be attained. A solution which contains H_2PtCl_6 equivalent to 0.1 gm. of Pt per cc. is a suitable one to employ.

Properties of Potassium Chloroplatinate. At a temperature of 20° one part of this compound requires about 98 parts of water, or 26,400 of 80 per cent alcohol, or 42,600 of absolute alcohol for complete solution. Ammonium chloroplatinate, which may be formed by the absorption of ammonium hydroxide from the atmosphere of the laboratory, is also extremely insoluble in these reagents. Both the hydrated and anhydrous sodium chloroplatinate and chloroplatinic acid are readily soluble in 80 per cent alcohol, but the chlorides and sulfates of sodium, potassium and magnesium are but slightly soluble in this reagent.

When made to separate by the evaporation of moderately dilute solutions, potassium chloroplatinate is coarsely crystalline and does not contain either combined or occluded water. It can be dried at a temperature of 135° without danger of decomposition or volatilization; at higher temperatures it is slowly decomposed into potassium chloride, chlorine and metallic platinum; it is not appreciably hygroscopic.

Development of the Lindo-Gladding Method. In 1881 Lindo* showed that potassium could be determined in solutions

* Chemical News, **44**, 77, 86, 97, 129 (1881), Bull. 7, Division of Chem. U. S. Dept. of Agriculture.

containing chlorides of sodium and potassium by evaporating to dryness with sufficient chloroplatinic acid to convert both elements into chloroplatinates, leaching out the sodium salt with strong alcohol and weighing the residual potassium salt. The method could not be used when SO_4 ions were present owing to the insolubility of sodium sulfate in alcohol and altho this ion could be removed by the use of barium chloride, and the excess of barium added could be removed by the use of ammonium carbonate this procedure greatly increased the length and difficulties of the method. In order to avoid these difficulties Gladding modified the method by washing the mixture first obtained with sufficient alcohol to remove all of the sodium chloroplatinate and chloroplatinic acid, and then with sufficient ammonium chloride solution to remove the sodium sulfate. This modification made it possible to apply the method to substances containing organic matter and ammonium salts, for, by evaporating with a slight excess of sulfuric acid and igniting gently, both classes of substances could be expelled without loss of potassium. It also made it possible to apply the method to substances containing magnesium salts as they are readily dissolved by solutions of ammonium chloride. The slight solubility of potassium chloroplatinate in the solution of ammonium chloride used was reduced to zero by saturating it with potassium chloroplatinate before use.

The method has been investigated by the Official Association of Agricultural Chemists and the exact details of the best method of procedure as applied to different classes of substances formulated. The outline given below is the official method* as applied to commercial potassium sulfate.

II. Outline of Method of Procedure

Preparation of Solution. Weigh out 10 gm. of the sample into a 500 cc. beaker, add 300 cc. of water, boil for a few minutes, then transfer to a 500 cc. graduated flask. Allow to cool, dilute to

* Bull. 107, Bureau of Chemistry, U. S. Dept. of Agriculture.

exactly 500 cc., mix thoroughly, filter about 300 cc. through a dry filter and preserve in a stoppered flask.

Separation of Potassium. Measure out 25 cc. of the solution by means of a pipet, add an equal volume of water, acidify with a few drops of hydrochloric acid, add 10 cc. of chloroplatinic acid (1 cc. = 0.1 gm. Pt) and evaporate on the water bath almost to dryness. Remove from the bath and add 25 cc. of 80 per cent alcohol, stir the mixture with a rod and break up any large masses, and after about five minutes decant off the clear liquid thru a weighed Gooch or alundum filtering crucible. Treat the residue with three 10 cc. portions of 80 per cent alcohol, stirring the mixture for several minutes after each addition and decanting as before. The last addition should remain colorless; if it acquires even a faint yellow color continue the washing. Finally transfer the residue to the filter by means of a stream of 80 per cent alcohol from a wash bottle.

Wash the residue on the filter five times with 10 cc. portions of ammonium chloride wash solution,* then with three 10 cc. portions of 80 per cent alcohol. Dry the crucible for a half hour at 100° and weigh accurately. Calculate and report the percentage of potassium as K_2O present. Save both the precipitate in the crucible and the filtrate and washings for the recovery of the platinum present.

III. Questions and Problems. Series 13

1. How much larger percentage error is involved in determining potassium when separated as $KClO_4$ than when separated as K_2PtCl_6, assuming that the sample contained 2 per cent of K, that one-half gram was used and that an error of 0.1 mg. was made in weighing both compounds?

2. What is the maximum error from solubility in the determination of K_2O in a substance which contains 20 per cent, assuming that all of the details outlined above are followed?

* Prepared by dissolving 100 gm. of ammonium chloride in 500 cc. of water, adding from 5 to 10 gm. of pulverized potassium chloroplatinate and shaking at intervals for from six to eight hours. Allow this mixture to settle over night, then filter. The residue may be used for the preparation of more solution.

3. Why is it desirable to evaporate on a *water bath* after adding the H_2PtCl_6? Why is it necessary to wash out all Na_2PtCl_6 and H_2PtCl_6 before washing with ammonium chloride? What might happen if the mixture was heated after alcohol was added? Why is it desirable to avoid changes in temperature while washing with the $(NH_4)Cl$ solution?

4. What modification of the method outlined would be necessary if the sodium and potassium were present as nitrates or phosphates respectively?

5. Outline a method for reconverting the platinum saved from the determination into H_2PtCl_6.

6. The potassium and sodium in a 0.5 gm. sample of K_2SO_4 are converted into a mixture of KCl and NaCl, which is found to weigh 0.35 gm.; the potassium is then separated as K_2PtCl_6, which is found to weigh 0.65 gm.; what percentages of K_2O and Na_2O are present?

7. Outline all the transformations necessary to carry out the determinations represented in the last problem.

CHAPTER XXX

DETERMINATION OF CRUDE FAT IN PEANUTS

I. Facts Upon Which the Determination Is Based

Chemical Nature of Fats and Oils. In the analysis of foods the different constituents are classified and determined with reference to the function they perform in the nutrition of the animal body. One of the most important of these groups consists of fats and oils; it includes a very large number of organic compounds, which are analogous to inorganic salts, in that they represent combinations of certain organic acids and glycerine, which acts as a trivalent base. The most important are olein, palmatin and stearine, which represent normal salts of oleic ($C_{17}H_{33}COOH$), palmitic ($C_{15}H_{31}COOH$) and stearic ($C_{17}H_{35}COOH$) acids, respectively. These compounds are not appreciably hygroscopic and do not absorb oxygen from the air, but the "drying oils," which are obtained when flax and certain other seeds are extracted, contain linoleic acid ($C_{17}H_{31}COOH$), and since this compound rapidly absorbs oxygen from the air such oils are difficult to weigh accurately.

Meaning of "Crude Fat." All of the compounds referred to above are distinguished by their extreme insolubility in water, and very slight solubility in alcohol; also by the readiness with which they are dissolved by ethyl ether, petroleum spirit, carbon disulfide and carbon tetrachloride. The remaining constituents of most food materials are not appreciably soluble in the four solvents last named. Many classes of food materials contain small amounts of other substances such as wax, resin, chlorophyll and various coloring matters, which are also more or less soluble

in these solvents, especially in ethyl ether. Long-established custom has led to the use of dry ethyl ether for the determination of this group of food constituents. Since the results obtained by extracting a material with ether may include small amounts of substances other than fat the result should always be designated as "crude fat" or "ether extract."

Purification of Ether. Unless especially purified ether contains both alcohol and water, and is then capable of dissolving appreciable amounts of certain sugars and other compounds which are not true fats. The alcohol can be removed by shaking the solvent with water and allowing the mixture to stand until it separates into two layers. The upper ethereal layer is then removed and the large amount of water which it contains separated by adding solid calcium chloride, and allowing the resulting aqueous solution of calcium chloride to separate out; the residual ether is then made anhydrous by adding metallic sodium and distilling. The purified solvent should boil at 35°. From 35 to 50 cc. are needed for each extraction where the continuous type of apparatus is used, but nearly 25 cc., which can be again used without further treatment, should be recovered when it is distilled from the fat.

Composition of Peanuts. The seeds of the peanut contain from 40 to 50 per cent of substances soluble in ether, nearly all of which are true fats. At least 80 per cent of the ether-soluble substances is tri-olein and the remainder is made up of the glycerides of stearic, arachidic ($C_{19}H_{39}COOH$) and lignoceric ($C_{23}H_{47}COOH$) acids. None of these substances absorb oxygen from the air at an appreciable rate and hence no difficulty is experienced in weighing the crude fat separated directly. On the other hand, the cellulose-containing residue, which remains after extraction, is appreciably hygroscopic.

Conditions Necessary for Complete Extraction. Ether penetrates cellular tissue even when dry but slowly, and still more slowly when the tissue is moist. If the sample contains much

moisture it is slowly taken up by the dry ether used, and gradually accumulates in the ethereal solution. Since the water cannot be easily distilled off from the crude fat without using an undesirably high temperature an appreciable error may result if the sample is not dried before it is extracted.

The large amount and liquid character of the fat present makes it impossible to grind these seeds in a mill, or to pass the ground pulp through a sieve. They can be crushed to a sticky mass in an agate mortar but this will still contain small lumps unless great care is taken. The pulp can be completely dehydrated by drying for an hour at 105° and the residue can usually be completely extracted in three hours if the apparatus used is efficient, and if not more than 3 gm. of sample is used. Time can be saved and greater accuracy assured if the extraction is continued for an hour, the almost completely extracted residue ground very fine and the extraction continued for an hour longer.

II. Outline of the Method of Procedure

Preparation of the Sample. Select eight or ten nuts of average size and maturity and remove the husks and the brown skin which envelops the seeds by means of a thin-bladed knife. Place the seeds on a porcelain plate or watch glass and cut into thin slices with a knife, then place in an agate mortar and crush to a pulpy mass till free from lumps. Weigh out 3 gm. of the sample into a closed, dry weighing bottle, place in a drying oven and keep at a temperature of 105° for an hour. Determine the loss in weight which results and calculate the percentage of water present.

The Extraction. Transfer the dried sample to a paper or alundum extraction shell and cover with a half-inch layer of cotton wool, which has been previously extracted with ether to remove the small amount of fat which it usually contains. Place the shell in an extraction tube similar to *B* of Fig. 40 or to Fig. 42. Weigh accurately a clean, dry fat-flask of 125 cc. capacity, add 35 cc. of pure dry ethyl ether and connect with the extraction tube by means

of an accurately-fitting cork stopper. Connect the extraction tube with the vertical condenser as shown in Fig. 45 and adjust the cork stoppers so that the flask rests directly on one of the iron heating plates, then start the water running thru the condenser. Close the switch which operates the heating device and after the ether begins to boil reduce the rate at which it boils, if this seems to be necessary, by interposing a thin sheet of asbestos over the heating plate. Adjust the end of the condenser so that all of the condensed ether falls inside the extraction shell and allow the process of extraction to continue for three hours.

Weighing the Crude Fat. Disconnect the extraction tube and flask from the condenser, remove to some distance from any source of heat and allow to drain for about five minutes. Disconnect the flask from the extraction tube and then connect the flask with one of the branches of the block-tin condenser tube. Place a receiving flask under the other end of the tin condenser tube and allow the ether to distil over until only about 2 cc. of yellow or brown oil remains. Then remove the flask and place in a water-jacketed oven, heat the water to boiling and keep at this temperature for an hour. Draw a current of dry air thru the flask by means of an aspirator until the residue gives no odor of ether. Allow the flask to cool and weigh accurately. Calculate the percentage of crude fat in the dried sample and in the original selected nuts.

CHAPTER XXXI

ANALYSIS OF BLACK POWDER

I. Facts Upon Which the Analysis Is Based

Composition. "Black powder" designates a mixture of charcoal, sulfur and either sodium or potassium nitrate which is largely used as an explosive, especially for blasting. Such mixtures are easily resolved into their essential constituents by first leaching out the soluble salts with water, then extracting the sulfur by means of carbon disulfide and assuming that the residual solid is charcoal. Altho the different ingredients are ground very fine, and intimately incorporated in the mixture, the solvents named readily act upon it since the charcoal makes the mixture porous, and there are no cell membranes thru which the solvents must pass to bring the soluble constituents into solution.

II. Outline of the Method of Analysis*

Determination of Moisture. Weigh out 2 gm. of the sample on a 3-inch watch glass, spread out as a thin layer and dehydrate, either by allowing to remain in a desiccator which contains concentrated sulfuric acid, for a period of three days, or by heating in an oven at 70° for several hours or until the weight remains constant. The temperature must be kept low to avoid any possibility of volatilizing some of the sulfur. Calculate the percentage of water lost.

Determination of Nitrates. Weigh out 10 gm. of the crushed sample into a Gooch crucible, which is designed to be used in a

* Bull. 51 of the U. S. Bureau of Mines by Walter O. Snelling and C. G. Storm.

Wiley extraction apparatus (see Fig. 41), weigh accurately and connect with a suction flask in the usual manner. Wash with at least 200 cc. of warm water added in quantities of about 10 cc. at a time, and test the last washings for nitrates by removing a few drops and adding at least an equal volume of strong sulfuric acid in which a few crystals of diphenylamine have been dissolved. This test will yield a deep blue color if even traces of nitrates are present. When all the nitrates have been leached out, remove the crucible, dry at 70° until the weight is constant and calculate the percentage of nitrates present from the difference between the total loss in weight and that due to the moisture originally present in the sample.

Determination of Sulfur. Place the crucible containing the residue from the last determination in a Wiley extraction apparatus and extract with about 35 cc. of recently distilled carbon disulfide for about one hour. Remove the crucible, allow most of the carbon disulfide to evaporate spontaneously, dry to constant weight at 70° and calculate the percentage loss as sulfur.

Determination of Charcoal and Ash. Calculate the percentage of charcoal from the weight of residue left in the crucible. Burn off the organic matter in the crucible, weigh the residual ash and calculate the percentage present.

SECTION V

PARTITION PROCESSES

CHAPTER XXXII

GENERAL FEATURES OF PARTITION PROCESSES

Consulate Liquids. When two liquids, which do not react with each other chemically, are mixed, one or more liquid phases, depending on the specific properties of the two liquids, may result. With certain pairs of liquids an infinite number of homogeneous solutions representing every possible ratio of the two constituents can be prepared; this is true of the liquids, alcohol and water. With other pairs of liquids the possibilities are limited; either liquid may become saturated with respect to the other, and if a greater amount of one liquid than is required to saturate the other is added, a new liquid phase separates. One of the resulting liquid phases usually contains a relatively large amount of the first liquid but is saturated with the second; the other usually contains a relatively large percentage of the second liquid but is saturated with the first. If small amounts of water are successively added to ether, and the mixture is shaken after each addition, a single phase containing a relatively large amount of ether is first obtained, but when the amount of water added exceeds 3 per cent by volume of the ether used, a second phase containing about 90 per cent of water separates. The addition of further quantities of water does not change the composition of either phase, but increases the amount of the water-rich phase at the expense of the ether-rich phase, and if a sufficient amount is added

will cause the entire disappearance of the latter. The addition of still further quantities of water merely increases the percentage of water in the water-rich phase.

Many pairs of liquids, such as kerosene and water, are so slightly soluble in each other that the addition of a very small amount of one liquid to the other at once produces two distinct phases, whose composition is practically the same as that of the pure solvents. Any pair of liquids which exist as independent phases after being shaken together and allowed to stand until equilibrium has been attained are spoken of as "consolute" liquids. The mutual solubility of two consolute liquids is affected very greatly by temperature changes. Increasing the temperature usually increases their mutual solubility and may cause them to become soluble in any proportions whatever, that is, may result in the disappearance of one of the two phases.

The Distribution Coefficient. When a small amount of a third substance is added to a system consisting of two consolute liquids, the whole shaken for some time, and allowed to stand until perfect equilibrium has resulted, the added substance, or a certain part of it, distributes itself between the two phases. The ratio of the concentration of the dissolved substance in one phase to the concentration in the other is a definite quantity, which is independent of the magnitude of the concentrations concerned, provided the dissolved substance does not dissociate and does not form molecular aggregates. This ratio can be easily determined experimentally and is known as the "distribution coefficient." Its value is affected to some extent by temperature changes. If the two liquids are but slightly soluble in each other, and if the added substance is much more soluble in one than in the other the value of the distribution coefficient will be either very large or very small, depending upon which of the two solutions concerned is taken as the standard of comparison. If, however, the two liquids possess a more nearly equivalent solvent power for the added substance, or if the two liquids dissolve one another to a large

extent, so that the composition of the two resulting liquid phase does not greatly differ, the value of the distribution coefficien becomes more nearly equal to unity.

Fig. 46.— Separatory Pipet

The Separation of Consolute Liquids. The tw liquid phases which make up a consolute mixtur can be mechanically separated by a variety of de vices. The simplest method is to insert a pipet o a tube, similar to the one shown in Fig. 46, into the mixture till its end is slightly above the plane separating the two layers, to draw the upper layer into the tube by suction, and transfer the liquid to another vessel. The separation thus effected is always imperfect as it is impossible to remove all of the upper layer without also removing some of the lower layer, but this error is comparatively small if the area of the containing vessel at the point of contact of the two layers is small.

A much more satisfactory device is a "separatory funnel," one of the many forms of which is represented in Fig. 47. This is provided with a glass stopper and a side tube, which can be closed with the finger or a good cork, so that the two consolute liquids can be shaken together vigorously. The lower of the two resulting layers can then be allowed to drain into another vessel by opening the glass stopcock at the bottom of the funnel. The inaccuracy of the separations made with such a device is due almost wholly to the small volume of the heavier liquid which adheres to the inner surface of the tube below the stopcock; for this reason this tube should be made as short as possible and of such a diameter that capillarity does not prevent it from discharging readily after the stopcock has been closed.

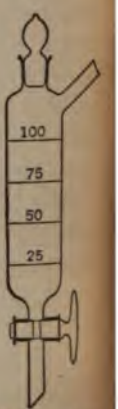

Fig. 47.— Separatory Funnel

Difficulties arise in the separation of two consolute liquids when one or both liquids show a tendency to "emulsify," that is, to

form an intimate mixture composed of small bubbles of the two liquids, which do not segregate except after very long standing. Instances occasionally arise in which this difficulty is sufficient to make the process concerned an impracticable one. The presence of any finely divided solid matter always retards and may prevent an entirely satisfactory segregation of the two liquids.

General Theory of Partition Processes. Iodine is much more soluble in the liquid carbon tetrachloride than in water and these two liquids are but slightly soluble in each other. As a consequence of these facts the distribution coefficient of iodine between the consolute liquids which result when carbon tetrachloride is added to an aqueous solution of iodine has at ordinary temperatures the value 85. This means that every unit volume of the carbon tetrachloride-rich phase will contain eighty-five times as much iodine as each unit volume of the water-rich phase. The total amount of iodine separated from an aqueous solution by this treatment would also depend on the volume of the aqueous, as compared with that of the carbon tetrachloride phase. Suppose, for example, it is assumed that the aqueous solution has a volume of 100 cc. and contained 0.2 gm. of iodine, that 50 cc. of carbon tetrachloride is added, and that the changes in volume which result after equilibrium has been established are insignificant. If x represents the weight of iodine in the resulting aqueous phase $0.2 - x$ must represent the weight of iodine in the carbon tetrachloride phase. The distribution coefficient would require that

$$\frac{x}{100} : \frac{0.2 - x}{50} :: 1 : 85.$$

When this expression is solved for x the latter is found to have the value 0.0046, that is, the weight of iodine in the aqueous solution is reduced to 4.6 mg. by this treatment.

If now the carbon tetrachloride solution is separated from the mixture, and the residual aqueous solution is again treated with 50 cc. of carbon tetrachloride a further quantity of iodine will be

taken up by the latter. If y represents the weight of iodine left in the aqueous solution after this second treatment, the distribution coefficient would require that

$$\frac{y}{100} : \frac{0.0046 - y}{50} :: 1 : 85.$$

The value of y calculated from the expression is found to be 0.0001016.

The calculation shows then that practically all of the iodine can be separated from the aqueous solution by two treatments with 50 cc. portions of carbon tetrachloride. It can be readily shown that the use of only 75 cc. of this liquid in three 25 cc. portions would have left only 0.018 mg. of iodine in the aqueous solution and in general, several treatments with small amounts of carbon tetrachloride is more efficient and economical than fewer treatments with larger amounts. It is also obvious that the smaller the volume of the solution from which the substance is to be determined is separated, the greater the efficiency of the process.

In general, the theory of partition processes shows a close analogy to that already developed in discussing the washing of precipitates, but unlike the latter it does not involve the use of assumptions which are never actually realized. Further emphasis should be laid, however, on the qualification already noted, namely, that the value of the distribution coefficient may change with varying concentration. This may result from the effect of varying concentration upon the degree of ionization or of hydration, or upon the nature of the substances actually present in the solution concerned.

CHAPTER XXXIII

DETERMINATION OF NICKEL IN NICKEL STEEL

I. Facts Upon Which the Determination Is Based

Composition of the Sample. Alloys of nickel and iron, which contain from 1 to 14 per cent of nickel, are frequently used for structural purposes where extreme hardness and toughness are demanded, and where the importance of these factors warrants the extra cost of such an alloy. They usually contain small amounts, up to 1 per cent, of combined carbon, very small amounts of silicon, sulfur and phosphorus and sometimes appreciable amounts of manganese and copper.

Altho nickel hydroxide is readily soluble in an excess of ammonium hydroxide this reagent cannot be used to effect a quantitative separation of nickel from iron, unless the process is repeated several times, or unless the percentage of iron present is very small, owing to the occlusion of nickel by ferric hydroxide. The partition process devised by J. W. Rothe is an extremely convenient and rapid method for making this separation.

Theory of the Separation. Anhydrous ferric chloride, unlike the chlorides of aluminum, nickel, cobalt, chromium, manganese, zinc and copper, is readily soluble in ethyl ether. If, however, ether is added to an aqueous solution of ferric chloride very little iron is taken up by the resulting ethereal solution unless a large concentration of hydrochloric acid or some soluble chloride is also present. It is probable that only unionized ferric chloride is appreciably soluble in ether, and that the element cannot be separated by the use of ether unless the ionization of the ferric chloride is repressed by the addition of hydrochloric acid. The

best results are obtained when the iron solution treated contains from 20 to 25 per cent of this acid.

The value of the distribution coefficient which is concerned here is not constant but varies with the temperature and the concentration of both acid and ferric chloride in the aqueous solution; under favorable conditions it may attain a value of 100. The values for the distribution coefficients of the chlorides of the metals named above, except possibly copper, are represented by extremely small fractions.

Conditions Necessary for the Separation. The rate at which iron was removed from an aqueous solution, which had a volume of 20 cc. and contained in addition to 20 per cent of hydrochloric acid 0.2054 gm. of iron as ferric sulfate, by successive treatments with 25 cc. portions of ether, is shown in the following results.

Iron removed by first treatment	0.1964 gm.
Iron removed by second treatment	0.0075 gm.
Iron removed by third treatment	0.0016 gm.
Iron removed by fourth treatment	0.0007 gm.
Iron removed by fifth treatment	0.0002 gm.

Since ferrous salts are not appreciably soluble in ether all of the iron must be kept in the ferric condition during the separation. As ether reduces ferric salts appreciably at a temperature slightly above the normal the mixture must be kept cold. It is further necessary to keep the concentration of all anions except chlorine low; if such anions are present they may keep some of the iron in such a form that it is not easily taken up by the ether.

Determination of the Separated Iron. Most of the ether ient in the ethereal solution can be recovered for subsequent tions by distilling in a suitable apparatus; were it not so of the method would often be prohibitive. The last e driven off by evaporating in an open vessel; the iron en reduced during the distillation and evaporation ed before it is precipitated.

Determination of the Separated Nickel. The decomposition voltage of the nickel ion is about 0.22 volt higher than that of the hydrogen ion. It can be rapidly and completely separated in a dense form from a neutral solution of the double oxalate, or from solutions of the sulfate to which a large excess of ammonium hydroxide has been added. In the presence of the NO_3 ion a small amount of nickel oxide, which is not easily redissolved, may separate at the anode. The precipitated metal is not dissolved appreciably by the ammoniacal solution and it is not easily oxidized.

II. Outline of Method of Procedure

Preparation of the Solution. Weigh out 2 gm. of the sample, which should be in the form of drillings or shavings, into a 300 cc. beaker, add 20 cc. of dilute hydrochloric acid, 5 of dilute nitric acid, cover with a watch glass and warm the mixture until the alloy is dissolved. Remove the watch-glass cover and evaporate the solution cautiously to avoid loss from spattering until a thick syrupy liquid or solid residue remains. Add 10 cc. of concentrated hydrochloric acid to the residue and evaporate as before; finally dissolve the residue in 10 cc. of dilute hydrochloric acid, dilute to 20 cc., filter off the small residue of silica and carbon on a 7 cm. filter and wash free from soluble salts, using the smallest necessary amount of cold wash water.

Separation of the Iron. Concentrate the filtrate to a volume of 10 cc., allow to cool and then transfer the solution to a 100 cc. separatory funnel with the aid of 10 cc. of dilute hydrochloric acid and 50 cc. of ether. Place both glass and cork stoppers in the funnel, cool the latter under a stream of water from the tap, shake cautiously once and release the excess of pressure created in the funnel by cautiously opening the cork stopper. Replace the cork stopper, again cool the funnel and shake vigorously for about three minutes. Support the funnel in a vertical position by means of a clamp and allow it to stand until the plane separating the two consolute liquids is clearly defined. Remove the cork stopper

and cause the aqueous phase to drain into the beaker previously used, allowing sufficient time to permit the aqueous phase to flow down the inner surface of the funnel and several drops of the ethereal phase to flow through the stopcock; then rinse off the lower end of the funnel with 2 or 3 cc. of water. These precautions become necessary for the purpose of rinsing every drop of the aqueous phase out of the funnel before attempting to remove the ethereal phase. Allow the ethereal phase to flow into a 200 cc. Erlenmeyer flask, rinse off the inner and outer surfaces of the tube below the stopcock with 3 to 5 cc. of water, then close the stopcock and set the flask aside. Transfer the aqueous solution in the beaker to the funnel with the aid of 25 cc. of ether and again mix and separate the ethereal layer. Connect the Erlenmeyer flask containing the combined ether extracts with a condenser and carefully distil off the ether, which can be used for subsequent determinations.

Separation of Last Traces of Iron. Add cautiously 5 cc. of concentrated sulphuric acid to the aqueous solution and warm gently until the ether present is expelled, then heat nearly to the boiling point and evaporate the solution until fumes of sulphur trioxide appear; next add 50 cc. of water, and digest until soluble salts are dissolved, then add 5 cc. of hydrogen peroxide to oxidize any iron which may have been reduced by the ether, heat to the boiling point and add an excess of ammonium hydroxide, that is, sufficient to impart a strong odor to the solution. Keep the solution at or near the boiling point for a few minutes, then filter off the precipitated iron and manganese on a 7 cm. filter and wash with the smallest necessary amount of hot water.

Determination of Nickel. Ignite and weigh accurately a clean platinum electrode, preferably of gauze. Place the electrode and a platinum spiral in the nickel solution, add 20 cc. of dilute ammonium hydroxide and make the proper connections with the terminals of a storage battery. If a gauze electrode has been prepared use a current of one ampere and allow the action to con-

tinue for at least fifteen minutes after the solution has become colorless. If a foil electrode has been prepared, it will be preferable to use a current of one half ampere only. Remove the cathode, wash in alcohol, dry at 100° and weigh. Calculate the percentage of nickel present. Remove the nickel from the cathode by allowing it to stand in a cylinder of strong nitric acid for twenty minutes and rinse off the acid with water.

III. Questions and Problems. Series 15

1. Calculate the values of the distribution coefficient for iron in the ethereal as compared with the aqueous phase at different concentrations from the data given on page 226.

2. Discuss the factors to which the changes in the values of this distribution coefficient are due.

3. A solution, which has a volume of 100 cc. and contains 0.4 gm. of $HgBr_2$, is treated successively with 20 cc. portions of benzene; if the distribution coefficient, that is $(HgBr_2)$ in $H_2O \div (HgBr_2)$ in C_6H_6, has the value 0.88, how many treatments are needed to reduce the amount of $HgBr_2$ to 0.1 mg.?

4. Write out a probable reaction for the reduction of ferric chloride by ether.

5. Suggest a probable effect of the presence of alcohol in the ether used for this separation.

6. What objections are there to precipitating the iron by means of ammonium hydroxide without previous oxidation?

7. Explain how nickel might separate at the anode during electrolysis and how NO_3 ions could favor the separation.

8. Would you expect the electrolytic determination of nickel to be affected by the presence of Co, Cu, Zn, Pb or Ag?

CHAPTER XXXIV

DETERMINATION OF CAFFEINE IN TEA

I. Facts Upon Which the Determination Is Based

Properties of Caffeine. The stimulating properties of tea and coffee are due for the most part to caffeine. This compound is represented by the formula $C_8H_{10}N_4O_2$, but it crystallizes with one molecule of water, which it begins to lose when heated to 110°. It belongs to that class of organic compounds which, owing to their weakly basic properties, are known as alkaloids. It begins to be appreciably volatile at 100°, melts at 225°, and can be sublimed without decomposition. It is soluble in about seventy-four parts of water, eight of chloroform and 2270 of ether. The salts which it forms with acids are more soluble in water than the free base.

Properties of Chloroform. One volume of chloroform requires nearly 183 volumes of water to dissolve it and the composition and properties of the consolute liquids formed when chloroform and water are mixed are essentially those of the pure components. Pure chloroform has a specific gravity of 1.526, it boils at 61° and its vapor is not inflammable; although it is an expensive reagent it is easily recovered and purified after use.

When caffeine is in equilibrium with chloroform and water the concentration in the chloroform layer is about thirteen times as great as in the aqueous layer. Altho this ratio is not very large it is so much larger than the ratio representing the distribution of inorganic salts between chloroform and water that caffeine can be easily separated from these salts by a partition process.

Composition of Tea Leaves. Tea contains in addition to from 1 to 5 per cent of caffeine, soluble inorganic salts, tannic acid,

coloring matter and small amounts of essential oils and organic acids. If the leaves are extracted with a sufficient amount of hot water all of the caffeine and most of the tannin, inorganic salts and organic acids are brought into solution. If the aqueous solution is treated with a sufficient amount of a solution of basic lead acetate the tannin and organic acids form insoluble lead salts, but the caffeine remains unprecipitated. The excess of lead acetate necessarily added can be separated by passing hydrogen sulfide through the solution, and the excess of hydrogen sulfide used can be boiled off.

Sources of Error. The small amount of caffeine present in tea makes it desirable to use several grams of the sample for the determination. The residue which remains after the extraction occupies a large volume and is difficult to filter and wash thoroughly. The precipitate of lead salts is also very bulky and forms a dense, impervious coating on the filter, which is difficult to wash. These errors are made as small as possible by weighing out about 5 gm. of the sample and, after digesting with water and separating the impurities, diluting to 500 cc., allowing the insoluble residue to settle and removing an aliquot part of the clear solution. This procedure involves a positive error since it is assumed in the subsequent calculations that the total volume of the solution was 500 cc. Altho a rough estimate of the volume occupied by the solid matter could be made and a correction introduced the process involves other negative errors, and a better result is obtained if the error is disregarded. Even where the greatest care is exercised the percentage error of the method is comparatively large.

II. Outline of Method of Procedure

Preparation of Aqueous Solution. Prepare the sample by crushing the leaves in an agate mortar till fine enough to pass thru a forty-mesh sieve. Weigh out 5 gm. of the sample, transfer to a 500 cc. graduated flask, add 400 cc. of water, heat slowly to the boiling point, taking care to prevent the mixture from boiling

over, and keep slightly below this temperature for a half hour. Cool the mixture to the temperature of the room and add slowly and with constant agitation 4 cc. of a solution of basic acetate of lead;* this should be sufficient to precipitate all of the tannin and coloring matters present. Dilute the mixture to exactly 500 cc., mix thoroughly and allow to stand until the solid matter present settles.

Remove by means of a pipet 20 cc. of the clear solution and allow it to pass thru an 11 cm. filter into a clean 200 cc. graduated flask but discard the filtrate thus obtained since the paper may have absorbed an appreciable amount of caffeine. Remove and filter further quantities of the solution until the flask is filled to the 200 cc. mark. Transfer the 200 cc. of filtrate to a 400 cc. beaker and pass hydrogen sulfide thru the solution until the precipitated lead sulfide becomes granular. Filter into another 400 cc. beaker, wash with a small amount of cold water, evaporate the solution to 100 cc. and allow to cool.

Separation of Caffeine. While waiting for the solution to evaporate, clean a 100 cc. Erlenmeyer flask dry in an air bath, allow it to cool in the balance room for at least half an hour and weigh accurately, using a glass counterpoise of about the same surface area.

Transfer the aqueous solution to a 200 cc. separatory funnel, add 20 cc. of chloroform, place both stoppers in the funnel and shake vigorously for three minutes. Support the funnel in a vertical position by means of a clamp, remove the cork stopper, place the previously weighed flask under the funnel and by carefully manipulating the stopcock allow the chloroform solution to run into it until the plane dividing the two liquids barely reaches the stopcock. Rinse off the lower end of the funnel with a few cc. pure chloroform added from a pipet and receive the

* by boiling 430 gm. normal lead acetate, 130 gm. litharge and water for an hour, allowing to cool and settle, and diluting until the sp. gr. is 1.25.

rinsings in the flask. Repeat the treatment with two more 20 cc. portions of chloroform.

Weigh accurately 1 or 2 inches of fine platinum wire and add to the flask. Connect the flask with a condenser by means of a glass tube and cork stoppers, start the water running through the condenser and cautiously distil off the chloroform until only a few drops of solution remain but avoid heating the flask much above the boiling point. The platinum wire should reduce the tendency of the solution to boil over materially. Return the distillate obtained to the stock bottle for future determinations.

Again extract the aqueous solution with three 20 cc. portions of chloroform, receiving the chloroform solution in the Erlenmeyer flask previously used and again distil off the chloroform.

Disconnect the flask from the condenser while still warm, introduce a glass tube, which is attached to an aspirator or water pump, to within a half inch of the bottom of the flask and draw air thru it for several minutes. Place the flask in an air bath heated to 75° for a half hour, again draw air thru it, allow to cool and weigh. The separated caffeine should consist of fine needle-like crystals of a nearly white color. Calculate the percentage present.

III. Questions and Problems. Series 16

1. Calculate the weight of caffeine which should be removed by each successive treatment of the pure aqueous solution, assuming that the weights and volumes used correspond exactly to those called for in the method outlined and that the sample contains 3 per cent of caffeine.

2. Calculate, as in the previous problem, the weights of caffeine which should be removed, assuming however that 1 cc. of the chloroform solution is left with the mixture after each treatment.

3. What compounds would you expect to find in the aqueous solution finally left from the determination of caffeine in tea?

4. What methods could you use to test the purity of the caffeine finally separated from the tea?

5. Is it at all probable that any of the caffeine would remain in the aqueous solution as a salt of hydrogen sulfide?

SECTION VI

GENERAL FEATURES OF VOLUMETRIC PROCESSES

CHAPTER XXXV

THEORY OF VOLUMETRIC PROCESSES

Fundamental Definitions. Volumetric analysis is that branch of quantitative analysis in which the amount of an element or compound, which is present in the substance submitted to analysis, is calculated from the volume of some reagent of known strength that is found to be necessary to complete a reaction with the element or compound being determined. A reagent especially prepared for making such a determination is known as a "standard solution." The value of this solution may be expressed either in terms of the number of grams of reagent actually present in a unit-volume, or in terms of the number of grams of any substance with which the reagent in one unit-volume reacts. The process of determining the volume of standard solution necessary to complete a reaction with a solution of the substance which is being analyzed, and in general the process of comparing the relative strengths of two solutions which react with each other chemically, is designated as "titrating."

The essential difference between gravimetric and volumetric processes consists in the substitution of a measurement of a standard solution for a determination of the weight of a precipitate, or of some product, which is separated from the substance being analyzed. Since volumetric processes necessarily involve calculating the magnitude of a weight, which corresponds to the weight

of precipitate or other product separated in a gravimetric process, they are virtually indirect methods of carrying out gravimetric processes.

Reactions Suitable for Volumetric Processes. Volumetric processes are usually based upon definite chemical reactions but only a limited number of reactions can be employed in making volumetric determinations. In general only those reactions which take place completely and instantaneously when equivalent amounts of the reacting substances are present are suitable for volumetric processes. For this reason reactions which result in the formation of new phases, or which give rise to products which are but slightly ionized, are largely used. A number of reactions which are sufficiently complete but not instantaneous become so upon the addition of a slight excess of the reagent used for the preparation of the standard solution. Such reactions are sometimes used as the basis of volumetric processes by the method of "back titration." In employing this device a slight excess of the standard solution is added, and the excess added is then titrated with a second standard solution, which reacts completely and instantaneously with the standard solution first employed. If the volumetric relation between the two standard solutions has been previously determined, the proper correction for the excess of standard solution first added is easily made.

Determination of the End-point. A second requirement, which reduces still further the number of reactions which can be used for volumetric determinations, is that some method can be devised to determine the point at which the amount of standard solution added is equivalent to the substance being titrated. As this point is approached certain of the physical and chemical properties of the solution change very rapidly in some cases there is a marked change in the color or electrical conductivity of the mixture, in others a precipitate may begin to form or may just cease to form, in still others the addition of another reagent, that is, an "indicator," causes a decided color change to take place.

The point at which a sufficient amount of the standard solution has been added to make these changes recognizable is known as the "end-point" of the titration. The difference between this point and the point at which an equivalent amount of the standard solution has been added, that is, the true end-point, must be small if the process is to be sufficiently accurate.

Theory of Indicators: First Case. Whenever an indicator is used, the physical change which is recognized is the result of a chemical reaction, in which the indicator itself is one of the active reagents. The indicator may react either with the substance being determined or with the standard solution employed in making the determination. In the latter case the reactions concerned may be represented by the following equations, in which X represents the substance being determined, R the reagent in the standard solution being used, and I the indicator employed:

$$(1) \quad X + I + R \rightarrow RX + I,$$

$$(2) \quad I + R \rightarrow IR,$$

$$(3) \quad IR + X \rightarrow RX + I.$$

The appearance of the end-point is here dependent upon the concentration of IR which should remain equal to zero as long as an appreciable concentration of X is present, but should increase in direct proportion to the amount of R added as soon as the concentration of X has been reduced to zero. In other words, reaction (1) must be completed before reaction (2) begins to take place, but reaction (2) must take place promptly, even when the concentrations of I and R are very small.

It is further necessary that in case a small amount of the compound IR has been formed during the earlier part of the titration, which may readily result from imperfect stirring and consequent accumulation of R in the upper layers of the solution, it should react with X according to equation (3), thus preventing the appearance of false end-points. Reaction (3) is also a direct

measure of the preponderance of reaction (1) over reaction (2) in the presence of X, that is, it insures the completion of (1) before (2) begins to take place.

It is evident, therefore, that the closeness of the agreement between the end-point actually recognized and the true end-point depends upon the values of the equilibrium constants of the three reactions concerned.

A second factor which is of some importance is the amount of indicator used. In those cases in which the end-points obtained depend upon a change from one specific color to another the two colors often tend to mask one another and give rise to a series of indeterminate transition tints. It is then desirable that the entire amount of indicator present should be completely transformed into the compound possessing the different color by the slightest possible excess of the titrating solution; in such cases only a small amount of indicator may be used.

If, however, the solution of the indicator is colorless, and the addition of an excess of the standard solution produces a specific color, a relatively large amount of indicator may sometimes be used to advantage. Increasing the concentration of the indicator favors the completion of reaction (2) but inhibits reaction (3). If, therefore, the equilibrium constant for (2) is somewhat small and that of (3) is sufficiently large, an increase in the amount of indicator used should increase the accuracy of the process. On the other hand if the reaction constant for (3) is too small and that of (2) is sufficiently large, a decrease in the amount of indicator used should increase the accuracy of the process.

Theory of Indicators: Second Case. If the indicator used reacts with the substance being determined the series of reactions concerned may be represented as follows:

$$(4) \qquad X + I \rightarrow IX,$$
$$(5) \qquad X + IX + R \rightarrow RX + IX,$$
$$(6) \qquad IX + R \rightarrow RX + I.$$

The appearance of the end-point is here dependent upon the concentration of I, which should remain equal to zero as long as an appreciable concentration of the excess of X is present. The accuracy of the process is determined largely by the magnitude of the three equilibrium constants concerned.

The Advantages of Volumetric Processes. Volumetric processes can usually be carried out much more rapidly and often demand less experience and skill than the corresponding gravimetric processes. The time needed to make the actual titration is usually a few minutes only but the necessity of removing interfering substances and of transforming the substance to be determined into the most suitable form often increases the time required for the entire analysis to several hours. Many are more accurate than the corresponding gravimetric processes but in other cases the reverse is true. They avoid the errors which are involved in making an actual separation, that is, the errors resulting from solubility, from occlusion or from other difficulties which yield an impure product, and from actual mechanical losses. On the other hand they necessarily involve certain errors in the preparation and measurement of the standard solution used and in the determination of the end-point of the reaction upon which the process depends.

Principle of Compensating Errors. A principle which can be used to great advantage in volumetric processes is that of counteracting the errors involved in the actual determination by equal errors in the standardization of the solution used. Assuming that there is always a discrepancy between the true and the observed end-point, it will generally be true that this discrepancy will be constant so long as the conditions remain constant. If the solution is standardized under exactly the same conditions as those which must obtain in the actual determination, practically all ›rs are eliminated as the standard solution used becomes merely ɜtrument by means of which the strengths of two solutions ıme substance, one representing a known amount of a pure

compound and the other the solution of unknown concentration, are compared. Considered from this point of view it is preferable to standardize the solution by comparing with a known weight of the substance being determined, and wherever it is possible to use the same solution for the determination of a number of substances, strict accuracy would demand that the solution be re-standardized for every one of the substances for which it is to be used.

Determination of Standard Solution Used by Weight. — When results of extreme accuracy are required, or when the volume of standard solution used is so small that the percentage error involved in measuring it is large it may be found advantageous to determine the amount of standard solution used by weight. When this procedure is adopted the solution should be standardized in a similar manner, that is, its value should be ascertained in terms of the weight to which one gm., rather than one cc., is equal. A special form of apparatus, which can be conveniently attached to the beam of the balance and weighed before and after the titration, is used to contain the standard solution. There is no gain in using standard solutions in this manner unless the accuracy with which the end-points of the process used can be determined approaches that with which the weights of the solutions used are determined.

CHAPTER XXXVI

MEASUREMENT OF THE SOLUTIONS USED IN VOLUMETRIC DETERMINATIONS

I. Sources and Methods of Avoiding Errors

Volumetric Apparatus. The accuracy of volumetric determinations depends in part upon the accuracy attained in the measurements made and necessitates the use of certain special forms of apparatus.

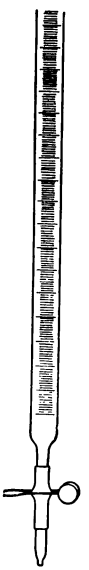

Fig. 48.—Mohr Buret

Burets are calibrated glass tubes of uniform, small diameter, designed to measure variable amounts of liquids delivered by them, when supported in a vertical position. The delivery of the liquid which is being measured is controlled in the form first used by Geissler (see Fig. 49), by a glass stopcock, and in the form first used by Mohr (see Fig. 48), by a rubber joint which connects the end of the tube with a glass nozzle, and is provided with a pinchcock or a screw clamp. The former has the disadvantage of requiring the use of some lubricant, such as a mixture of beeswax and vaseline, to prevent leakage, and of being more expensive and more easily broken. The latter has the disadvantage that the rubber connection is acted upon to some extent by solutions of strong alkalies and by

Fig. 49.—Geissler Buret

certain oxidizing agents, which may reduce the concentrations of the solutions measured in them appreciably.

The total capacity of the burets usually employed is either 100, 50, 25 or 10 cc.; the 50 cc. buret should be graduated to read tenths of a cubic centimeter and its diameter should be small enough to permit of estimating fiftieths of a cubic centimeter with reasonable accuracy. Burets of smaller capacity should be made of tubes having a still smaller diameter in order to make measurements with a corresponding degree of accuracy. Since two readings are involved in each measurement the maximum possible error in the use of a 50 cc. buret should not exceed one twenty-fifth of a cubic centimeter which corresponds to one-eighth of one per cent when the amount measured is as much as 50 cc.

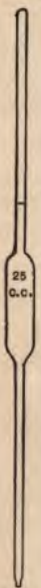

Fig. 50.—Pipet

Pipets are tubes of much smaller bore than burets, designed to measure definite amounts of liquid only. They are usually provided with an enlargement at their center, as in Fig. 50, which greatly increases their capacity, and a single mark near the upper end, which indicates the point to which they must be filled to deliver the volume for which they are calibrated. Sometimes they are calibrated by means of two marks, one above and the other below the enlargement, and in this case the value of the pipet is determined by the volume of liquid delivered during the passage of the meniscus from the upper to the lower mark. The so-called measuring pipets (Fig. 51) lack the enlargement at the center, and are calibrated like burets; they are rarely used for amounts greater than 10 cc. The form of

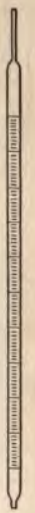
Fig. 51.—Pipet

the pipet should be such as to permit of a free flow of the liquid over its entire inner surface when held vertically, and the orifice should be small. The time required for the delivery of the liquid from a 50 cc. pipet should not be less than 20 seconds; from a 10 cc. pipet it should not be less than 10 seconds. Where properly used the error involved in the measurement with a 25 cc. pipet should not exceed one one-hundredth of a cubic centimeter. They are to be preferred to burets wherever it is possible to use them, on account of the greater ease and accuracy with which they can be manipulated.

Fig. 52. — Graduated Flask

Graduated flasks (Fig. 52) are flat-bottomed, and have a long narrow neck. They are usually calibrated to contain a definite volume, but may be calibrated to deliver that volume. The diameter of the neck should be small as compared with its capacity; that of a 1000 cc. flask should not exceed 20 mm.; that of a 100 cc. flask should not exceed 10 mm.

The uncertainty involved in the use of a 1000 cc. flask should not exceed a tenth of a cubic centimeter; for a 100 cc. flask it should not exceed two one-hundredths of a cubic centimeter.

Graduated cylinders are cylindrical glass tubes provided with an enlarged base or foot and with a lip for pouring. They are calibrated to indicate the varying amounts of liquid which they can contain and are employed for rough measurements only.

Error from Parallax. Errors may result from inaccuracies in reading the level of the liquid in the apparatus used. Unless the liquid being measured is intensely colored the lowest point on the curve of the meniscus forms the most satisfactory point of reference, with which to compare the graduations on the apparatus. Since this point lies at the center of the tube the error from parallax, especially where the tube is of large diameter, must be avoided.

The simplest method of doing this is to hold the tube so that its main axis is perfectly vertical, and make all measurements with the eye held at such a level that the line of sight makes an angle of 90° with the axis that is, the measurement is made from the point at which the plane tangent to the meniscus at its lowest point and perpendicular to the axis of the tube cuts the wall of the apparatus.

A number of devices may be employed to assist in maintaining the eye at the proper position. A piece of looking glass may be held in contact with the back of the tube and the level of the eye shifted till the lowest point of the meniscus, the graduation nearest to it, and the reflection of that graduation in the mirror are all on the same line, as represented in Fig. 53. A piece of stiff paper with a perfectly straight edge may be folded around the tube in such a manner that the two edges of the paper, the one being at the front, the other at the back of the tube, and the lowest point of the meniscus are all in line with one another.

Fig. 53.—Use of a Mirror in Reading Buret

A more convenient device is found in the Schellback burets (see Fig. 54) and pipets in which a strip of dark blue or black glass, and two adjoining strips of white enamel glass are introduced at the back of the tube directly opposite the graduations. If the level of a liquid in a tube of this kind be observed the dark strip seems to contract to a point just opposite the meniscus, as shown in the sketch. If the eye is held at the proper level this becomes an exceedingly sharp point of reference from which to compare the graduations on the tube.

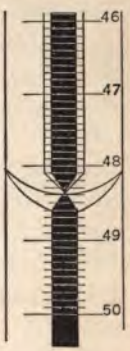

Fig. 54.—Schellback Buret

Still another device employed with burets only is a cylindrical glass float (Fig. 55) provided with an encircling line etched on its outer surface. By comparing the projection of the plane of this circle with the graduations on the tube an exceedingly accurate reading can be made. Unless the float is properly adapted in form and size to the bore of the buret, capillary action retards its movement as the level of the liquid changes, and gives rise to large errors.

Fig. 55.—Float for Buret

If the liquid being measured is intensely colored the circle formed by the uppermost points on the curve of the meniscus forms the most satisfactory plane of reference with which to compare the graduations on the tube.

Error from Drainage. When a liquid is permitted to pass out of a buret somewhat rapidly small amounts adhere to its inner surface, and some of it gradually flows down and unites with the liquid still remaining in the buret. The rapidity with which the level of the liquid in the buret attains its ultimate position depends upon the viscosity of the solution, the area and form of the surface drained, and the rapidity with which the solution has been permitted to flow from the tube. The viscosity depends in turn upon the chemical nature, concentration and temperature of the solution. In order to avoid errors from this source a sufficient interval must elapse between the time at which the flow from the apparatus is stopped, and the time at which the reading is made. The minimum value of this time interval is easily ascertained by a series of simple experiments.

In the use of pipets both the drainage from the inner surface, and the capillary action at the nozzle have to be considered, and a nite method of procedure must be adopted, both in calibrating pet and in its subsequent use. The conditions which yield uniform results are obtained when the nozzle of the pipet

is permitted to touch the wall of the receiving vessel while the liquid is flowing from it, and to remain in contact with it for 20 seconds after the main part of the liquid has been delivered; the attempt to blow out the few drops, which are retained by the nozzle as the result of capillary action, is not to be recommended.

Error from Water in the Apparatus. It is usually necessary to rinse measuring apparatus with water before using and the amount of water retained by the apparatus may effect an appreciable change in the concentration of the solution measured. The error can be avoided by drying the apparatus before use, but a more convenient method is to rinse it out with some of the solution which is to be measured and discard the rinsings. The amount of liquid used for this purpose should be at least 10 per cent of the total capacity of the measuring vessel, and should be made to flow over the entire inner surface by repeatedly shaking or by inverting the apparatus.

Error from Changes in Temperature. A change in temperature affects both the size of the vessels used and the density of the liquid measured. The first effect is practically constant for temperatures ranging from zero to 100°. For glass vessels of the usual form this so-called "coefficient of cubical expansion" has the value 0.000025, which represents the increase in the capacity of the vessel for an increase of one centigrade degree.

The second effect is not constant even over small ranges of temperature and varies greatly with the liquid concerned; it is much greater than the effect on the containing vessel. All organic liquids show a large expansion as compared with water. The expansion of dilute aqueous solutions, such as are used in most volumetric determinations, does not differ greatly from the xpansion of pure water.

The actual error which results from the use of a piece of graduated apparatus at a temperature which differs from that at which has been calibrated is due to the difference between the effect the liquid and the effect on the containing vessel. It is a

simple task to calculate, from the coefficient of cubical expansion of glass and from a table showing the expansion of water for different temperatures, a series of factors which represent the number by which the observed volume should be multiplied to correct for departures in temperature from that for which the apparatus was calibrated.

Error from Variations in the Unit of Volume Employed. The choice of a unit of volume is determined solely by convenience, but it is essential that the same unit be employed in all the operations involved in any one determination. The standard liter, that is, the volume occupied by a kilogram of water, when weighed in a vacuum and measured at a temperature of 4° is manifestly inconvenient. The so-called "Mohr unit" which is the volume of a kilogram of water when weighed in the air with brass weights at a temperature of 17.5° is more convenient, since these conditions do not differ greatly from those normally prevailing in the laboratory. Other units involving measurements at temperatures of 15°, 16° or 20° have been used by other chemists. The exact value of any of these units, in terms of absolute metric units, can be determined by calculating the changes in volume which take place when a flask containing sufficient water to counterbalance a kilogram brass weight at 4° in a vacuum is heated to a temperature corresponding to the unit of volume concerned, and when an amount of water sufficient to counterbalance the buoyant effect of the air, which results from allowing air at atmospheric pressure to replace the vacuum, is added.

Much of the calibrated apparatus sold by manufacturers bears no mark by means of which the unit volume represented can be determined, and even when this is clearly designated the percentage error represented may be large. It is not advisable, therefore, to se any piece of calibrated apparatus, when the work in hand ands great accuracy, until its actual value has been ascertained analyst.

book the volume occupied by that amount of water which

nterpoises a kilogram of brass when measured either at 15° or ferably) at 20° are the units adopted. The factors by which volumes found at temperatures ranging from 10 to 25° must be tiplied in order to obtain the true volume when measured in se units are given in the following table:

Temperature of actual measurement	Factor for apparatus calibrated at 15°	Factor for apparatus calibrated at 20°
10	1.00047	1.00124
11	1.00040	1.00117
12	1.00032	1.00109
13	1.00023	1.00100
14	1.00012	1.00089
15	1.0	1.00077
16	0.99987	1.00064
17	0.99972	1.00049
18	0.99956	1.00034
19	0.99940	1.00018
20	0.99923	1.0
21	0.99904	0.99981
22	0.99884	0.99961
23	0.99861	0.99941
24	0.99841	0.99919
25	0.99820	0.99897

II. Detailed Description of Method for the Calibration of Volumetric Apparatus

Cleaning Graduated Apparatus. Carefully clean a 50 cc. et and two pipets, preferably of 10 and 25 cc. capacity. If ir inner surfaces are contaminated with a film of organic matter, er will adhere to them in streaks and drops. These impurities uld be removed by rinsing either with a strong solution of ium hydroxide or with a cleaning mixture made by saturating uric acid of 1.6 specific gravity with sodium dichromate; in eme cases it may be necessary to allow the apparatus to stand night in a cylinder filled with this solution. If the buret is he Mohr type the rubber connection should be removed since

it is injured by contact with this solution. This connection sl be pliable and not too long and the glass tip should have a round opening. The pinchcock should be strong enough to vent leakage even when the buret is full of water.

Reading the Buret. Practice reading the buret partly with water until you can read its level accurately to a fiftieth cubic centimeter by the use of one of the devices describe page 243. Determine the minimum length of time which i be allowed for drainage by filling with water to the zero point allowing the water to flow rapidly from the delivery tube its level reaches one of the lowest graduations, and noting changes in level at intervals of one minute from the tim closing the pinchcock.

Calibration of the Buret. Weigh accurately to 0.01 gm. a 35 cc. weighing bottle or a small beaker with a watch-glass c Fill the buret with distilled water whose temperature does differ by more than 1° from either 15° or 20°, depending u whether the normal temperature of the laboratory corresp more nearly to 15° or 20°. Raise the delivery tube of the b until nearly horizontal and while still holding in this position c the pinchcock until the air-bubble, which is sometimes pre has been driven out then lower the delivery tube and again c the pinchcock until the lowest point of the meniscus corresp exactly with the zero point of the buret.

Place the delivery tube of the buret inside the weighing bo open the pinchcock, and allow 5 cc. of water to pass thru Close the bottle and weigh as before, then read and record exact position of the water in the buret. Continue to remove weigh 5 cc. portions of the water until 25 cc. have been remo Empty the water from the bottle, dry and again weigh, and t calibrate the remaining 25 cc. portion of the buret.

Prepare a table, of which one column represents the weight water delivered between the zero point and the ten other po at which readings were made; a second column, the correspond

readings; and a third column, the figures in column one diminished by those in column two. The figures in the third column represent the corrections to be added or subtracted from the apparent readings. If any of these errors amounts to as much as 0.05 cc. calibrate the buret in the neighborhood of the point giving this error at intervals of 1 cc.

Calibration of Pipets. Weigh to 0.01 gm. a clean and dry weighing bottle of about 30 cc. capacity. Suck up pure water whose temperature is either 15° or 20° into the 25 cc. pipet until the level of the liquid is above the mark on the stem. Close the upper end of the pipet with your finger, which should be perfectly dry, and then by gently releasing the pressure allow water to flow out until the lowest point on the curve of the meniscus corresponds to the mark on the pipet. Place the nozzle of the pipet in contact with the inner surface of the weighing bottle and allow the water to flow into it and to drain for 20 seconds. Close the weighing bottle and weigh to 0.01 gm.

Calibrate the 10 cc. pipet in the same manner.

Calibration of Flasks. Clean a 100 cc. and a 250 cc. flask and rinse with distilled water. Insert a long piece of glass tubing which is attached to a foot bellows, or other device for producing a blast of air, into the 250 cc. flask, hold the latter in an inclined position with the neck down and slowly heat the body of the flask by means of a smoky flame rotating the flask about its axis until drops of moisture can no longer be recognized in the interior of the flask. Allow it to cool, clean the outside surface, and weigh accurately.

Fill the flask with water at the standard temperature until the lowest point on the meniscus corresponds to the mark on the neck of the flask. Place on a balance designed to carry a load of at least 500 gm. and weigh to 0.01 gm. Subtract the weight of the flask from the weight last obtained to find the capacity of the flask.

Calibrate the 100 cc. flask in a similar manner.

III. Questions and Problems. Series 17

1. How many absolute metric units are there in the (20°) unit of volume used in the calibrations made, assuming that the specific gravity of water at 20° is 0.99823, the specific gravity of brass is 8.3 and that one liter of air weighs 1.2 gm.? *Ans.* 1.0028.

2. What weight of water would you use if you desired to calibrate a liter flask to represent an absolute metric unit, but found it necessary to do the work at a temperature of 20° and under ordinary atmospheric conditions?

3. A solution which has been standardized at a temperature of 15° by the use of a buret which was also calibrated for this temperature was found to contain 0.02 gm. of hydrochloric acid per cc.; if some of this solution is measured out of the same buret at a temperature of 10°, what weight of hydrochloric acid is present in each cc. as measured out?

4. In preparing a one-tenth normal solution of silver nitrate (which should contain 0.010788 gm. of Ag per cc.) 5.7 gm. of silver was weighed out, dissolved and diluted to 500 cc. in a graduated flask. The solution in this flask was emptied into a bottle, which had not been dried and which contained 0.5 cc. of water adhering to its sides, and further 0.4 cc. of the silver solution was left adhering to the flask. If 28.36 cc. of water was added to the bottle and the mixture shaken, what relation would the resulting mixture bear to one-tenth normal strength? *Ans.* 0.99916.

5. The volume of water which remains adhering to a 500 cc. flask is 0.4 cc., how large a volume of a solution which is to be measured in it should be added to the flask for the purpose of rinsing it out so that the concentration of the original solution shall not be changed by more than one-hundredth of one per cent? *Ans.* 2.8 cc.

CHAPTER XXXVII

YSTEMS USED IN THE PREPARATION OF STANDARD SOLUTIONS

The Unitary System. The general expression by means of which the result of a volumetric determination is calculated is:

$$\frac{\text{Vol. of standard solution}}{\text{Wt. of sample used}} \times f \times 100 = \text{percentage desired},$$

in which f is the weight of substance being determined, which reacts with one cubic centimeter of the standard solution used. It is clearly advantageous to use a standard solution of such a concentration that f is an integer. If, for example, a solution of sodium chloride is being employed for the determination of silver, it is desirable to make $f = 0.01$, and if so each cubic centimeter of sodium chloride solution must contain

$$0.01 \times \frac{\text{Mol. Wt. of NaCl}}{\text{At. Wt. of Ag}}, \text{ or } 0.00542 \text{ gm.}$$

Even when the process concerned is a complicated one, that is, involves the use of a series of reactions, the standard solution used for the final titration can be made to conform to this system, which can be conveniently designated as the "unitary system." If, further, the weight of sample used for the analysis is exactly one hundred times as great as the value of 1 cc., every cubic centimeter used for the determination represents 1 per cent of the substance being determined, and the percentage present corresponds to the number of cubic centimeters used in making the determination. If, for instance, 1 gm. of alloy is weighed out for the determination of silver and the latter is determined by titrating with a sodium chloride solution containing 0.00542 gm. per

cubic centimeter the percentage of silver in the alloy corresponds to the number of cubic centimeters used.

So long as standard solutions are to be used for the determination of only one substance the unitary system is the most convenient one to employ, but it is often desirable to use such solution for the determination of a variety of substances, and in such instances the necessary calculations possess the desired simplicity for only one of the substances concerned. If, for example, the solution used for the determination of silver is also used for the determination of mercury by means of the reaction $Hg_2(NO_3)_2 + 2\,NaCl \rightarrow Hg_2Cl_2 + 2\,NaNO_3$ the value of f becomes

$$0.01 \times \frac{\text{At. Wt. Hg}}{\text{At. Wt. Ag}} = 0.01859.$$

It becomes necessary therefore, when this system is used, to prepare a separate solution for every substance determined; if a very large number of determinations of these substances are to be made this may be a desirable thing to do, but frequently the extra labor involved in preparing and using the several different solutions more than offsets the gain in making the calculations.

General Features of the Normal System. When the standard solution is to be employed only occasionally, and for the determination of a variety of substances, it is preferable to make use of the so-called "normal system." The essential idea upon which this system is based is to use such concentrations that equal volumes contain equivalent amounts, of the different reagents and therefore that a mixture composed of equal volumes of any two such solutions which react with each other will not contain an excess of either reagent. In order to prepare such a series of solutions it is necessary that the standard volume, usually the liter, should contain amounts of the active reagents which bear a simple relation to the molecular weights of the compound concerned. The exact value of this relation may be conveniently estimated by comparing the chemical activity of the molecule with that of

the hydrogen atom as a unit or standard. A normal solution is then defined as one which contains in a liter an amount of the active reagent chemically equivalent to 1.008 gm. of hydrogen. Thus a normal solution of any acid, which contains a single replaceable hydrogen atom, and which is used in a reaction involving simple neutralization, must contain as many grams of that acid as there are units in its molecular weight. A normal solution of any base must be equivalent to a normal solution of any acid; and hence, if the base contains a single hydroxyl group, the liter should contain an amount corresponding to its molecular weight expressed in grams; if it contains two hydroxyl groups it should contain one-half as many grams as there are units in its molecular weight.

Where the reagent is used in a reaction involving oxidation, or reduction, or precipitation, exactly the same principle is used. In every case the oxidizing, or reducing, or replacing power of the molecule concerned, as compared with the oxidizing or reducing or replacing power of the hydrogen atom, determines the number by which the molecular weight must be divided to give the normal value. This number will be designated in this book as the "equivalency." Further details as to the method of computing the normal values of different reagents will be discussed as the different processes are described.

Normal Values Dependent Upon the Reaction Concerned. It should be especially noted that the normal value of a substance may vary according to the type of reaction in which it is used. Thus the normal value of a solution of oxalic acid is determined by dividing its molecular weight by two, no matter whether used as a neutralizing, a reducing, or a precipitating agent; whereas the normal value of nitrous acid is the entire molecular weight, when used as a neutralizing agent, but is one-half its molecular weight when used as a reducing reagent. Further than this the same reagent may be used in two reactions which belong to the same type and have a different normal value for each. Thus phosphoric acid may be used in reactions in which it acts as a

monovalent or a divalent acid; in the former case its normal value is the entire molecular weight, in the latter case it is one-half its molecular weight.

Advantage of the Normal System. Since a normal solution of any reagent must, according to definition, be chemically equivalent to a normal solution of any substance with which it reacts, every cubic centimeter of such a solution must be equivalent to as many grams of that substance as are present in a cubic centimeter of a normal solution of that substance. In other words the value of 1 cc. of a standard solution, in terms of any substance with which it reacts, is determined by dividing the molecular weight of the substance by one thousand times its equivalency. The general expression for the calculation of the results of a volumetric determination, where a normal solution is used then becomes:

$$\frac{\text{Vol. of solution used}}{\text{Wt. of sample}} \times \frac{M}{1000 \times E} \times 100 = \text{per cent of substance,}$$

where M is the molecular weight and E is the equivalency of the compound determined.

The advantage of the system is most striking where the process concerned is an indirect one, that is, where the method involves the use of a series of reactions. In such cases the usual stoichiometric method requires a separate calculation, involving one multiplication and division, for every reaction concerned. By the use of the normal system it is possible from a mere inspection of the reactions concerned, to calculate the value of the solution being used in terms of the substance being determined, by a single division. For example, potassium bitartrate may be determined by dissolving in water, neutralizing and precipitating as calcium tartrate, filtering off the precipitate and converting into calcium carbonate by igniting in an open crucible and titrating the resulting carbonate with standard hydrochloric acid. The reactions involved are:

(1) $$C_4H_5KO_6 + KOH \rightarrow C_4H_4K_2O_6 + H_2O,$$

(2) $$C_4H_4K_2O_6 + CaCl_2 + 4\,H_2O \rightarrow C_4H_4CaO_6 \cdot 4\,H_2O + 2\,KCl,$$

(3) $$2\,C_4H_4CaO_6 \cdot 4\,H_2O + 5\,O_2 \rightarrow 2\,CaCO_3 + 6\,CO_2 + 12\,H_2O,$$

(4) $$CaCO_3 + 2\,HCl \rightarrow CaCl_2 + H_2O + CO_2.$$

An inspection of these reactions shows that each molecule of bitartrate yields one of neutral tartrate, one molecule of neutral tartrate yields one of calcium tartrate, one of calcium tartrate yields one of calcium carbonate and one of calcium carbonate is equivalent to two of hydrochloric acid. Since the hydrochloric acid contains one replaceable hydrogen atom its equivalency is one, hence the equivalency of the calcium carbonate is two and also the equivalency of potassium bitartrate, when determined by this process, is two. The formula for the calculation of the result of the determination is:

$$\frac{\text{Vol. of sol.}}{\text{Wt. of sample}} \times \frac{\text{Mol. Wt. of } C_4H_5KO_6}{2 \times 1000} \times 100 = \text{per cent of } C_4H_5KO_6.$$

Use of Solutions Which Bear a Simple Relation to Normal Strength. Normal solutions are too concentrated to give the best results, and it is customary to prepare solutions which bear a simple relation to normal strength, that is, are either one-half, one-fifth or one-tenth normal. The results obtained by the use of such solutions are correctly calculated by introducing the factors one-half, one-fifth or one-tenth in the formula given above.

Even where the solution has not been prepared to bear a simple relation to normal strength this method of calculation may still be employed to advantage. The relation of any solution to normal strength can be calculated by dividing the number of grams of active reagent in 1 cc. by the number of grams present in 1 cc. of normal solution of that reagent; or, it may be determined by dividing the number of grams of any substance with which 1 cc. reacts by the number of grams in 1 cc. of a normal solution of that substance. The resulting factor representing the exact relation of the solution to normal strength is then used in the above formula just as the simpler factors one-half, etc.

SECTION VII

VOLUMETRIC PROCESSES INVOLVING PRECIPITATION

CHAPTER XXXVIII

DETERMINATIONS WHICH DEPEND UPON THE USE OF A STANDARD SOLUTION OF SILVER NITRATE

I. Theory Upon Which the Methods Depend

Reactions Between Silver and Halogen Ions. The addition of a solution of silver nitrate to one containing a soluble salt of hydrochloric, or hydrobromic or hydriodic acid yields silver halides, whose solubilities are so small that their dissociation can be considered to be practically complete; further, when these reactions are used in volumetric analysis the concentrations of the soluble silver salt and of the soluble halide are so small, at least in the neighborhood of the true end-point, that their dissociation can be considered to be complete; hence the concentration of the halogen left unprecipitated in these reactions depends upon the solubility product of the silver halide formed. As all three of these halides are very slightly soluble the reactions concerned in forming them are sufficiently complete to justify using them as the basis of volumetric processes. There is further, in dilute solutions at least, no tendency for the formation of complex ions or the separation of salts of abnormal composition.

Determination of End-Points Without an Indicator. When silver chloride first separates as a precipitate it is finely divided and a very minute quantity of it can be recognized; if the solution

containing it is shaken vigorously the precipitate coagulates, leaving a supernatant liquid which is perfectly bright and clear. Hence if a soluble chloride is titrated with silver nitrate and the mixture well shaken in a stoppered bottle after every addition of silver solution, the point at which the addition of a further quantity of solution fails to produce a further quantity of precipitate can be recognized. Under certain conditions this method of determining the end-point admits of a very high degree of accuracy and is widely used in determining the fineness of silver bullion. As it is a somewhat tedious method and demands skill and experience a less accurate but more convenient method, which depends upon the use of an indicator, is usually employed when the less valuable halogen is determined by the use of this reaction.

Determination of End-Points With a Chromate Indicator. The neutral chromate of silver has an intense red color, and altho its solubility is small, it is decidedly greater than that of the silver halides. These facts suggest the possibility of using a solution of a neutral chromate as an indicator in the titration of the halogens with a silver salt. The series of reactions concerned is represented by

$$(1)\qquad \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{Cl}} + \overset{+}{\mathrm{Ag}} + \overset{-}{\mathrm{NO_3}} \rightarrow \mathrm{AgCl} + \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{NO_3}},$$

$$(2)\qquad 2\overset{+}{\mathrm{Na}} + \overset{--}{\mathrm{CrO_4}} + 2\overset{+}{\mathrm{Ag}} + 2\overset{-}{\mathrm{NO_3}} \rightarrow \mathrm{Ag_2CrO_4} + 2\overset{+}{\mathrm{Na}} + 2\overset{-}{\mathrm{NO_3}},$$

$$(3)\qquad \mathrm{Ag_2CrO_4} + 2\overset{+}{\mathrm{Na}} + 2\overset{-}{\mathrm{Cl}} \rightarrow 2\,\mathrm{AgCl} + 2\overset{+}{\mathrm{Na}} + \overset{--}{\mathrm{CrO_4}}.$$

The process evidently corresponds to the first of the two general cases discussed in Chapter XXV. The changes which take place during the progress of the titration can be readily followed by means of some simple calculations.

When a very dilute solution of silver nitrate is slowly added to a solution containing both sodium chloride and a soluble chromate a very slight amount of silver solution is sufficient to produce a precipitate of silver chloride, that is, as soon as the concentration of the silver ion exceeds the quotient obtained by dividing the

mixture, the amount of AgCl and the extent to which it is coagulated, and the ability of the analyst to recognize slight color changes.

This discussion indicates that altho a relatively large amount of indicator should be used in the titration, moderately large variations in this amount produce a comparatively slight effect upon the final result. It is also evident that a personal factor is involved in the titration and it is desirable to eliminate this as far as possible by standardizing the silver solution with a known weight of a pure chloride and making all determinations under exactly the same conditions as were adopted in the standardization.

Effect of Acids Upon the Titration. Altho moderate concentrations of even largely dissociated acids do not affect reaction (1) appreciably very slight concentrations affect reaction (2) to such an extent as to make it impossible to determine the true end-point with even approximate accuracy. This can be explained by considering the reactions which take place when silver chromate is treated with nitric acid, namely,

$$(4) \qquad Ag_2CrO_4 + \overset{+}{H} + \overset{-}{NO_3} \rightarrow H\overset{-}{CrO_4} + 2\overset{+}{Ag} + \overset{-}{NO_3},$$

$$(5) \qquad 2\,H\overset{-}{CrO_4} \rightarrow \overset{--}{Cr_2O_7} + H_2O.$$

Both of these reactions have been studied quantitatively.* The equilibrium constant for (4), that is, $(H\overset{-}{CrO_4}) \div (\overset{+}{H})\,(\overset{--}{CrO_4})$ has the value 1.2×10^6 and the equilibrium constant for (5), that is, $(\overset{--}{Cr_2O_7}) \div (H\overset{-}{CrO_4})^2$ has the value 74. The combined effect of these reactions is to decrease $(\overset{--}{CrO_4})$ by an amount which nearly equals the total amount of hydrogen ion present. As the solubility product of $Ag_2Cr_2O_7$ has the value 2×10^{-7} there is but little probability that this salt will separate unless both $(\overset{+}{H})$ and $(\overset{+}{Ag})$ in addition to $(\overset{--}{CrO_4})$ are large. Still another effect results from the fact that Cr_2O_7 ions impart a red instead of a yellow color

* Sherrill, Jour. of Am. Chem. Soc., **29**, 1641 (1907).

to the solution and materially increase the difficulty of recognizing small amounts of Ag_2CrO_4.

The presence of small concentrations of hydroxyl ions is not objectionable provided the solubility product of silver hydroxide is not exceeded. If the solution is made neutral toward such an indicator as litmus or rosolic acid no difficulty from either H or HO ions will be experienced.

Reactions Between a Silver Salt and a Cyanide. When a silver salt is first added to a solution of a soluble cyanide a complex ion is formed; the process is represented by

$$(6) \qquad \overset{+}{Ag} + \overset{-}{NO_3} + 2\overset{+}{K} + 2\overset{-}{CN} \rightarrow 2\overset{+}{K} + Ag(\overset{-}{CN})_2 + \overset{-}{NO_3}.$$

The value of the equilibrium constant for this reaction, that is, $Ag(\overset{-}{CN})^2 \div (\overset{+}{Ag})\ (\overset{-}{CN})^2$ is 1×10^{21}, hence the amount of silver left in the form of a simple ion is extraordinarily small.

As the solubility product of $KAg(CN)_2$ is large no precipitate forms nor is there any other indication of the progress of the reaction. The solubility product of the salt $AgAg(CN)^2$ has the value 2.25×10^{-12} and as soon as sufficient silver has been added to complete reaction (6) a slight further addition brings about the reaction

$$(7) \qquad \overset{+}{K} + Ag(\overset{-}{CN})_2 + \overset{+}{Ag} + \overset{-}{NO_3} \rightarrow AgAg(CN)_2 + \overset{-}{NO_3} + \overset{+}{K}.$$

Determination of End-Point in Titration of Cyanides. When a soluble cyanide is titrated with a silver salt the point at which reaction (6) has been completed and (7) begins to take place is shown by the appearance of a white precipitate, that is, $AgAg(CN)_2$. Altho the solubility product of this salt is small it has the property of coagulating almost at once and small amounts of it are not readily recognized.

Silver iodide is less soluble and more difficult to coagulate than silver cyanide and when freshly precipitated an extremely small amount of it can be easily recognized. If a solution of silver nitrate is added to a solution containing both cyanides and iodides

silver iodide will not separate as long as ($\bar{C}N$) has an appreciable value, since the equilibrium constant for reaction (6) is 1×10^{21} whereas the solubility product of silver iodide has the value 1×10^{-16}; that is, unless the concentration of the iodide ion is very large. When the titration has been carried to the point at which ($\bar{C}N$) is extremely small ($\overset{+}{A}g$) begins to increase very rapidly and soon attains a value sufficient to cause either AgI or $AgAg(CN)_2$ to separate. As the solubility product of AgI is 1×10^{-16} and that of $AgAg(CN)_2$ is 2.25×10^{-12} the latter precipitate should not separate as long as a reasonably large concentration of soluble iodide is present. Experience shows that there is a very slight tendency for the separation of some silver cyanide with the iodide, but this tendency is entirely suppressed by the addition of a small amount of ammonium hydroxide. This is one of the most easily recognized and accurately defined end-points known.

Method of Preparing a Standard Silver Solution. Silver which is 999.5 fine can be obtained from dealers and an accurately standardized solution of silver nitrate can be prepared by weighing out the proper amount of metal, dissolving in nitric acid without loss and diluting accurately to the calculated volume. If the solution is to be used with the chromate indicator the excess of nitric acid used must be completely expelled or accurately neutralized. Complete expulsion cannot be assured unless the solution is evaporated to dryness and the residual salt heated to about 198°, that is, to the fusion point of the salt. As silver nitrate begins to decompose slightly above this temperature it must be heated with great care.

II. Preparation and Standardization of a One-Tenth Normal Solution of Silver Nitrate

Preparation of Solution. Weigh out accurately from 5.4 to 5.8 gm. of pure metallic silver, place in a casserole or porcelain dish, cover with a watch glass, and add 20 cc. of dilute nitric acid. If action does not begin to take place after a few minutes, or if it

becomes too slow, warm gently or add a small amount of strong acid. When the metal is dissolved rinse off the under side of the watch glass and set it aside, then place on the steam or sand bath and evaporate the solution to complete dryness. If the sand bath is used the mixture must be stirred during the later stages of the evaporation to avoid losses from spattering. Finally raise the temperature to the point at which the nitrate just fuses, noting that since the solubility curve terminates in the fusion curve and the molten nitrate forms a nearly colorless liquid this transition may escape recognition. The complete absence of white fumes when air is blown over the hot dish is sufficient evidence of the complete removal of nitric acid.

Allow the dish to cool, dissolve the salt in a little water and transfer the solution to a 500 cc. graduated flask, using the rinsings of the dish to dilute to exactly 500 cc. Place a cork in the flask and invert several times or until the mixture is homogeneous, then transfer to a clean glass-stoppered bottle, which has been allowed to drain for about five minutes. Calculate the volume to which the silver weighed out should be diluted to make the residual solution exactly one-tenth normal, that is, to make 1 cc. contain 0.010788 gm. of silver, and add to the bottle from a buret the necessary amount of water, then shake thoroughly. Test the solution with a piece of blue litmus paper for acidity; if it gives a perceptible reaction it must be neutralized by cautiously adding very dilute sodium hydroxide and the small amount of insoluble precipitate formed filtered off.

Standardization. Weigh out from 0.23 to 0.28 gm. of pure recently dried sodium chloride into a 200 cc. Erlenmeyer flask, add 35 cc. of water and one of a 5 per cent solution of pure potassium chromate. Rinse out a clean 50 cc. buret with 10 cc. of the silver solution and discard the rinsings, then fill to the zero mark.

Add the silver solution to the salt solution somewhat rapidly until the red precipitate which forms temporarily disappears

slowly, then add it more slowly until the mixture acquires a faint but permanent reddish tinge. If shaken vigorously the red chromate of silver may separate with the silver chloride instead of remaining suspended.

Calculate the weight of sodium chloride found to be equivalent to 1 cc. of the silver solution and divide by the weight of sodium chloride in 1 cc. of a normal solution of sodium chloride to obtain the normality factor.

III. Determination of Chlorine in Kainite

Preliminary Statements. The mineral kainite is found in the Stassfurt salt deposits, and is one of the important sources of potassium salts. It is sometimes rep esented by the formula $KCl \cdot MgSO_4 \cdot 6\,H_2O$, but it rarely corresponds exactly with this, and furthermore is usually associated with sodium chloride and other salts. Large amounts of it are ground and used directly as a fertilizer.

The Analysis. Weigh out from 0.5 to 0.8 gm. of the sample into a 200 cc. Erlenmeyer flask, add 50 cc. of water and titrate with the silver solution exactly as in the standardization. Calculate and report the percentage of chlorine present by making the proper substitutions in the general formula.

IV. Determination of Chlorine in Tap Water

Preliminary Statements. The percentage of chlorine in well or river water varies greatly and its determination often yields results which are of much significance in deciding whether a sample is suitable for domestic use, for irrigation or for the production of steam. Usually the amount present is relatively small and it is desirable to measure out from 200 to 500 cc. for the determination. The volume of silver solution required to produce a recognizable amount of silver chromate is much larger than in the ious titrations; it can be ascertained by determining the which must be added to an equal volume of distilled water,

to which some white precipitate such as zinc oxide or calcium carbonate has been added, to yield a mixture which after titration shows the same color change as the sample. The white precipitate is added to produce an effect similar to that produced by the silver chloride in the sample.

The Analysis. Test the sample for alkalinity by means of a piece of red litmus paper. Measure out exactly 250 cc. of the sample into a 400 cc. Erlenmeyer flask and if necessary neutralize by careful addition of very dilute nitric acid. Next add 1 cc. of the chromate indicator and titrate with the silver solution until a recognizable amount of silver chromate is produced, and set the flask aside. Measure out 250 cc. of distilled water, add 0.2 gm. of zinc oxide or calcium carbonate, and titrate this mixture with the silver solution until it shows a color exactly equal to that of the sample in the flask set aside. Subtract the volume used in titrating the distilled water from that used in titrating the sample and calculate the weight of chlorine corresponding to this volume of silver solution. Report results in terms of grams of chlorine per liter of water.

V. Determination of Potassium Cyanide in Commercial "Cyanide"

Preliminary Statements. The commercial "cyanide" which is so largely used for the extraction of gold and silver from their ores consists of a mixture of sodium and potassium cyanides together with small amounts of carbonates, chlorides, ammonium salts and hygroscopic water. As sodium and potassium cyanide are about equally efficient solvents for the treatment of gold and silver ores it is customary in the evaluation of such cyanides to determine the total cyanogen and to calculate the corresponding amount of potassium cyanide. As the cyanide is extremely hygroscopic it is somewhat difficult to secure an average representative portion of a large sample, unless a large amount is taken for the analysis dissolved in water and a fractional part of the

solution used for the analysis. Great care should be exercised in handling the sample as it is extremely poisonous.

The Analysis. Crush several pounds of the original sample until the particles do not exceed grains of wheat in size, place at once in a glass-stoppered bottle and rotate and shake the latter until thoroughly mixed. Add about 5 gm. of the sample to a weighing bottle and weigh accurately. Transfer the salt to a 250 cc. graduated flask, dissolve in water, dilute to exactly 250 cc. and mix thoroughly. Remove a 25 cc. pipet full of the solution to a 200 cc. Erlenmeyer flask, being very careful to avoid getting any of the solution into the mouth, add 5 cc. of dilute ammonium hydroxide, then 2 cc. of a 5 per cent solution of potassium iodide and finally titrate with the silver solution until a very faint but permanent turbidity, due to the formation of silver iodide, appears. The accuracy of the determination can be increased by holding the flask against a black background while determining the end-point. Calculate the percentage of potassium cyanide present from the volume of silver solution required, noting that E of the general formula has the value one-half.

VI. Questions and Problems. Series 18

1. What volume of a one-tenth normal solution of silver nitrate would be required to saturate 100 cc. of a solution which contained 0.3 gm. of potassium chromate with silver chromate, assuming that the solubility product of silver chromate is 1.70×10^{-12}? *Ans.* 0.01 cc.

2. If a standard solution of silver was used to titrate a solution containing bromine ions, what concentration of potassium chromate should be present in order to cause silver chromate to separate as soon as an equivalent amount of silver nitrate had been added, assuming that the solubility product of silver bromide was 0.49×10^{-14}? *Ans.* 3.5×10^{2}, which is impossible.

3. If solid silver nitrate was added to 100 cc. of a solution, which contained 0.2 gm. of potassium chromate and 1.64 gm. of sodium acetate, what weight of silver nitrate would have to be added before silver acetate would begin to separate, assuming that the solubility product of silver acetate was 3.48×10^{-3} and that all the salts concerned were completely dissociated?

4. The concentration of the chlorine ion in a solution which is saturated with AgCl and which has a volume of 100 cc. is 1×10^{-5}; what volume of a one-tenth normal solution of silver nitrate would it be necessary to add in order to reduce the concentration to 1×10^{-6}? *Ans.* 0.19 cc.

5. Calculate the solubility product of lead iodide, assuming that its solubility is 0.44 gm. per liter.

6. A solution of silver nitrate contains exactly 0.015 gm. of $AgNO_3$ per cc., and 24 cc. of it are required to precipitate the chlorine in 0.5 gm. of a sample which contains $BaCl_2 \cdot 2\,H_2O$; calculate by the general formula the percentage of this salt present.

7. It is found that 30 cc. of the solution referred to above are needed to react with the cyanide in 0.7 gm. of a sample which contains $Ca(CN)_2$; calculate in a like manner the percentage of this salt present.

8. The volume of tenth normal silver solution used in titrating 0.5 gm. of a sample of kainite is 35 cc.; if one drop (0.04 cc.) of this volume is used in producing a recognizable amount of Ag_2CrO_4, what percentage error and what departure from the correct result does it cause?

9. If the results obtained for the determination of potassium cyanide in commercial "cyanide" exceeded one hundred per cent, what explanation might be suggested?

CHAPTER XXXIX

DETERMINATION OF ZINC BY MEANS OF A SOLUTION OF POTASSIUM FERROCYANIDE

I. Theory Upon Which the Method Depends

The Reaction Concerned. When a dilute solution of potassium ferrocyanide is slowly added to a solution of a zinc salt a flocculent precipitate of a bluish color separates, but a point is finally reached at which the precipitate becomes pulverulent and pure white. The precipitate finally obtained contains both potassium and zinc, the relative amounts of which may vary according to the conditions under which the precipitate separates. It is not known whether a double ferrocyanide of zinc and potassium is formed or whether potassium ferrocyanide is adsorbed by the zinc ferrocyanide which first separates.

In devising a method for the determination of zinc based upon this reaction it is necessary to adopt certain standard conditions, and a preliminary study of the manner in which varying conditions affect the reaction is a necessary prerequisite to the intelligent use of the reaction. Under the conditions which are here adopted the reaction is represented with approximate accuracy by

(1) $2\,K_4Fe(CN)_6 + 3\,ZnCl_2 \rightarrow K_2Zn_3[Fe(CN)_6]_2 + 6\,KCl.$

Determination of the End-Point. When a soluble ferrocyanide is added to an iron salt a deep blue, or when added to a salt of copper, cobalt or uranyl a deep red-brown, precipitate separates. It is possible to recognize a smaller amount of a soluble ferrocyanide by means of a uranyl salt than of the other salts

mentioned, and these salts form the best indicators for this titration. The reaction with a uranyl salt is probably represented by

$$(2) \qquad 2\,(UO_2)(C_2H_3O_2)_2 + K_4Fe(CN)_6 \rightarrow (UO_2)_2Fe(CN)_6 + 4\,K(C_2H_3O_2).$$

If a solution of potassium ferrocyanide is added to one which contains approximately equivalent concentrations of salts of both zinc and uranyl both reactions (1) and (2) can be shown to take place, and further, if a solution containing zinc and potassium chlorides is added to a solution which contains suspended uranyl ferrocyanide the latter is not affected. This indicates that the factor which determines the completeness of the reaction

$$(3) \qquad 2\,(UO_2)_2Fe(CN)_6 + 3\,ZnCl_2 + 2\,KCl \rightarrow Zn_3K_2[Fe(CN)_6]_2 + 4\,(UO_2)Cl_2$$

has a comparatively small value or that the velocity is small. On the other hand, reaction (3) does not proceed in the reverse direction, at least when the time allowed is short, and a solution of a uranyl salt can be used to test a solution which is being titrated, for potassium ferrocyanide, since the addition of a uranyl salt will not produce a precipitate of uranyl ferrocyanide unless an excess of potassium ferrocyanide is present. In using a uranyl salt as an indicator, however, it is necessary to remove portions of the solution from time to time during the progress of the titration and bring it into contact with a drop of the indicator solution.

Since it may be necessary to make a large number of these tests before the true end-point is reached, and since that portion which is removed cannot be returned to the main solution without producing a permanent precipitate of uranyl ferrocyanide the total amount of zinc taken out may represent a rather large error. This error is small if the analyst has an approximate idea of the total amount of zinc present and can safely add sufficient ferrocyanide to precipitate most of the zinc before beginning to test

the solution. When the amount present is entirely unknown it becomes necessary to divide the solution into a number of fractional parts and use one of these for an approximate determination, that is, to titrate by the addition of 1 or 2 cc. of the standard solution at a time; a second portion is then titrated to within 1 or 2 cc. of the required amount at once and completed by the addition of 0.1 cc. at a time. This method of determining an end-point which involves the use of an "outside" indicator is necessarily tedious but is the best method known for this titration.

It is found that from 0.5 to 0.7 of the ferrocyanide solution usually employed must be added to 200 cc. of water before a clearly recognizable test is produced with the indicator. If all titrations are made with the same volume of solution the error from this source is constant, and if all the solutions titrated contain the same amount of zinc the error bears the same relation to the total amount of zinc represented. Suppose, for example, the ferrocyanide solution is standardized, by titrating a solution which contains 0.150 gm. of zinc and has a volume of 200 cc., and that 30 cc. are required to react with the zinc. The total volume of solution required would be 30.5 cc. and the apparent value of each cubic centimeter 150 ÷ 30.5, or 0.004918. If now this solution is used to titrate a zinc solution which has a volume of 200 cc. and contains 0.05 gm. a volume of 10.5 cc. would be required and the calculated amount of zinc would be 10.5×0.004918, or 0.0516 gm. That is, an error of 1.6 mg. results, which would have been avoided if 0.5 cc. had been subtracted from the volumes of ferrocyanide solution used in the two titrations.

Effect of Varying Temperature Upon the Process. In the experiments, the results of which are recorded below, a zinc solution containing 0.005 gm. of zinc per cc. was titrated with a ferrocyanide solution containing 21.6 gm. of $K_4Fe(CN)_6 \cdot 3\,H_2O$ per liter at varying temperatures.

The results show that altho the ratio between the volume of zinc solution used, and the volume of ferrocyanide solution needed

sol.	$(NH_4)Cl$	HCl (conc.)	H_2O	Temp.	Vol. of $K_4Fe(CN)_6$ sol.
	gm.	cc.	cc.	Degrees	cc.
)	5	5	140	20	25.5
)	5	5	140	50–45	29.85
)	5	5	140	80–75	29.85
)	5	5	140	100–95	30.02

ıct with it, decreases when the temperature is increased from o 100° it is constant between 45° and 80°. In the practical of this method it is very desirable to adopt among other lard conditions, a temperature at which the ratio is as nearly ant as possible, since it is not always convenient to maintain rticular temperature thruout an entire titration. It should e noted that at 20° it is much more difficult to recognize the end-point than at any of the higher temperatures. A tem- ure of 80° can be advantageously adopted for one of the lard conditions.

fect of Varying Concentrations on the Process. The effect rying the concentration of the zinc salt, while maintaining same concentration of hydrochloric acid and ammonium ide, is shown in the results of the experiments recorded in ollowing table:

l_2	$(NH_4)Cl$	HCl (conc.)	H_2O	Temp.	$K_4Fe(CN)_6$ used
	gm.	cc.	cc.	Degrees	cc.
)	1.25	1.25	12.5	80	29.5
)	2.50	2.50	55.0	80	29.70
)	3.75	3.75	97.5	80	29.75
)	5.0	5.0	140.0	80	29.80
)	7.50	7.50	225.0	80	30.01

slight increase in the volume of ferrocyanide solution used increasing dilution is undoubtedly due to the larger amount rrocyanide required to produce a sufficient concentration of

the latter to yield a recognizable test with the uranyl indicator. There is no reason to believe that the ratio here concerned varies, provided the concentration of the other reagents remains constant. Convenience alone should therefore determine the best volume to use for the titration. Since in the actual application of the method the zinc must usually be separated from other metals and a large volume of solution is necessarily obtained a volume of 200 cc. is a desirable standard to adopt.

Effect of the Hydrogen Ion on the Process. In titrating a solution of a zinc salt with a solution of a ferrocyanide the end-point is much more accurately determined when the solution contains a small amount of acid than when perfectly neutral. The presence of sufficient acid also assists in bringing about the change from a blue flocculent to a white pulverulent precipitate, which is a desirable feature. Further, when lead is present in the zinc solution the presence of sufficient acid suppresses the formation of insoluble lead ferrocyanide, and makes it possible to titrate zinc in the presence of this element.

The effect of varying concentrations of hydrochloric acid on the titration is shown in the following table:

$ZnCl_2$ sol.	$(NH_4)Cl$	HCl (conc.)	H_2O	Temp.	$K_4Fe(CN)_6$ used
cc.	gm.	cc.	cc.	Degrees	cc.
30	5	0	145	80	±29.4
30	5	1	144	80	±29.8
30	5	5	140	80	29.90
30	5	10	135	80	30.10
30	5	25	120	80	31.50
30	5	50	95	80	32.90

These results show a gradual increase in the volume of ferrocyanide solution required for the same amount of zinc with increasing ncentration of acid altho the rate of increase is not large. Both r large and very small amounts of acid greatly increase the

difficulty of obtaining accurate end-points and indicate the desirability of adopting for one of the standard conditions 5 cc. of the acid for each 200 cc. of solution.

Preparation and Standardization of the Solution. This method is very widely used for the determination of zinc in ores and alloys, and it is found desirable to make 1 cc. of the ferrocyanide solution used equivalent to 0.005 gm. of zinc, that is, to prepare it according to the unitary rather than according to the normal system. Under the conditions already adopted as standard, that is, where the temperature at the beginning of the titration is 80°, the volume before titration is 200 cc., and where 5 gm. of ammonium chloride and 5 cc. of concentrated hydrochloric acid are present it is found that a solution of potassium ferrocyanide containing 21.6 gm. of the crystallized salt per liter will precipitate 0.005 gm. of zinc per cc. The exact value of the solution should be determined by titrating against a known amount of zinc. Either pure metallic zinc or pure zinc oxide, which has been recently ignited to convert any zinc carbonate which it may contain into zinc oxide, is used for the standardization.

The ferrocyanide solution is not a very stable one and may show an appreciable change in standard even after standing for a week, which necessitates frequent restandardization. An appreciable tendency for the ferrocyanide to change into ferricyanide, which results in less clearly defined end-points, is also recognizable.

II. Application of the Method to the Analysis of Zinc Ores

Preliminary Statements. Most of the important ores of zinc contain that element as sphalerite (ZnS) or smithsonite ($ZnCO_3$), both of which are easilydissolved by concentrated hydrochloric acid; in certain classes of ores it is present as calamine ($Zn_2SiO_4 \cdot H_2O$), which is but slowly or imperfectly decomposed by treatment with acids and such ores must usually be fused with some

basic substance such as sodium carbonate to render them easily soluble.

All classes of zinc ores invariably contain silica or insoluble silicates, iron in the form of pyrites, and very often lead, copper, cadmium and manganese, also, as sulfides. As the zinc in such mixtures is frequently intimately associated with the other sulfides it is usually necessary to decompose these minerals, also, in order to insure complete solution of the zinc, which necessitates treatment with nitric as well as hydrochloric acid.

Separation of Zinc in Simple Ores. When the ore does not contain copper or cadmium, and where the percentage of iron is small as compared with the zinc, the latter can be separated with a sufficient degree of accuracy for the ferrocyanide titration by the use of ammonium hydroxide and bromine. The separation of zinc from iron by the use of ammonium hydroxide is unsatisfactory, owing to the occlusion of zinc by the ferric hydroxide precipitate, but where the total amount of iron does not exceed 0.1 gm. a double precipitation usually suffices to give a satisfactory separation. Manganese if present in small amounts is usually completely precipitated with the iron as the dioxide, if a moderate excess of bromine water is also added. The excess of bromine thus added to the zinc-containing filtrate must, however, be driven off by evaporation before titration with the ferrocyanide solution, as it readily oxidizes ferrocyanide to ferricyanide.

III. Outline of Method for the Preparation and Standardization of the Ferrocyanide Solution

Preparation. Weigh out 21.63 gm. of crystallized potassium ferrocyanide, dissolve in water and dilute to 1000 cc.

Titration of a Known Weight of Zinc. Ignite about 2 gm. of pure zinc oxide in a platinum or porcelain crucible for 20 minutes at a good red heat and then allow to cool. Weigh out 0.25 gm. the ignited oxide into a 400 cc. beaker, add 10 cc. of dilute hydrochloric acid and warm until dissolved. Neutralize the

solution with ammonium hydroxide, add 5 cc. of concentrated hydrochloric acid and then dilute to 200 cc. Heat the solution thus obtained to 80° and add somewhat slowly 38 cc. of the ferrocyanide solution. Complete the titration by adding the ferrocyanide solution in quantities of not more than four drops at a time, and after vigorous stirring bringing a drop of the mixture into contact with a drop of a 5 per cent solution of uranyl acetate, which has been previously placed on a white porcelain plate or a sheet of glazed white paper. The drop of solution taken for the test should be mixed thoroughly with the drop of indicator, but the rod should be wiped or rinsed off before it is again placed in the solution which is being titrated. The true end-point represents the point at which a slight but clearly defined brownish tinge can be recognized with certainty. The intensity of the color finally adopted as the true end-point should be carefully noted, and all subsequent titrations should be carried to the same color shade. As the intensity of this color increases on standing, an effort should be made to allow the same time interval to elapse between the first admixture of the two drops and the final decision as to whether the end-point has been reached.

Determination of Excess Required for the End-Point. To a second beaker add 10 cc. of dilute hydrochloric acid, sufficient ammonium hydroxide to neutralize it and then 5 cc. of concentrated hydrochloric acid. Dilute the mixture to 240 cc., heat to 80° and titrate with the ferrocyanide solution as before, noting that the absence of the white potassium-zinc ferrocyanide precipitate may decrease slightly the excess of ferrocyanide required to produce a color shade as intense as that adopted in the previous titration.

Calculation of Value of Ferrocyanide Solution. Subtract the volume of ferrocyanide solution used in this titration from that used in titrating the zinc solution. Calculate the weight of zinc equivalent to the zinc oxide weighed out and divide by the volume (corrected) of ferrocyanide solution used.

IV. Outline of Method for Determination of Zinc in an Ore Which Contains Neither Copper nor Cadmium

Decomposition. Weigh out 1.5 gm. of the finely ground sample into a 200 cc. beaker, add 10 cc. of concentrated hydrochloric acid, cover with a watch glass and warm gently until violent action ceases and hydrogen sulfide is no longer given off. Add 5 cc. of dilute nitric acid and again warm to insure complete decomposition of pyrite, which might otherwise retain some zinc, and also to effect complete oxidization of all the iron present. After violent action ceases remove the watch glass and evaporate almost to complete dryness, but avoid a temperature in excess of 100°.

Separation of the Zinc. Add to the residue 10 cc. of concentrated hydrochloric acid, slowly heat to the boiling point and then add 50 cc. of water. Heat the solution to the boiling point, add a moderate excess of ammonium hydroxide and then 10 cc. of bromine water and keep near the boiling point for about 5 minutes. Allow the precipitate of iron, manganese and gangue-matter to settle, then filter thru a small filter receiving the filtrate into a 250 cc. graduated flask, allow to drain and wash 4 times with 10 cc. portions of water. Replace the graduated flask by the beaker just emptied and pour over the filter sufficient warm dilute hydrochloric acid to change all of the ferric hydroxide into ferric chloride, then wash the filter free from iron. Dilute the solution in the beaker to at least 50 cc., heat to boiling and again precipitate with ammonium hydroxide and bromine water; filter and wash as before, receiving the filtrate in the graduated flask previously used. Add sufficient hydrochloric acid to this solution to make it slightly acid.

Division of Zinc Solution. Cool the solution in the flask to the temperature of the room and dilute with water until the liquid es the mark on the neck of the flask. Place a stopper in the the flask and mix its contents thoroughly by inverting the shaking vigorously several times. Rinse out a 50 cc.

pipet with some of the zinc solution and discard the solution thus used; then measure out two 50 cc. portions of the solution into 400 cc. beakers.

Titration of Zinc. Add to each of the 50 cc. portions of zinc solution 5 cc. of concentrated hydrochloric acid and dilute to 200 cc. Heat one of these solutions to 80° and titrate with the ferrocyanide solution adding 10 cc. before making the first test and then 1 cc. portions successively until an end-point is reached. Heat the second zinc solution to 80° and titrate with the ferrocyanide solution, adding 1 cc. less than the total amount used in the previous titration before making the first test and then $\frac{1}{10}$ cc. portions successively until an end-point is reached. Calculate the percentage of zinc present.

V. Questions and Problems. Series 19

1. What is the replacing power and the normal value of potassium ferrocyanide, when used to determine zinc by the reaction given on page 268?

2. In titrating a solution which has a volume of 200 cc. and contains 0.150 gm. of zinc 30 cc. of ferrocyanide solution are required to precipitate the zinc and 0.5 cc. to give an end-point with the solution; if 20.5 cc. are added before any tests are made with the indicator and then a test is made (necessitating the removal of 0.04 cc.) after each successive addition of 1 cc. portions of solution, how large a volume of ferrocyanide solution would actually be used in making the titration? *Ans.* 30.49 cc.

3. Should the delicacy with which the end-point is recognized be affected by the size of the drop removed for the test, assuming the volume of indicator used is not changed?

4. Explain the action of $(NH_4)HO$ and $(NH_4)Cl$ in the separation of iron from zinc. Could any other reagent be substituted (a) for $(NH_4)HO$, (b) for $(NH_4)Cl$?

5. Outline a method for the determination of zinc in an ore which also contains copper and cadmium.

SECTION VIII

VOLUMETRIC PROCESSES INVOLVING NEUTRALIZATION

CHAPTER XL

GENERAL THEORY OF NEUTRALIZATION PROCESSES

The Reactions Concerned. A large number of processes, which depend upon the use of a standard solution of an acid or a base, are included in this group: the most important are based upon reactions which involve simple neutralization. As shown on page 58 the equilibrium constants of such reactions can be calculated by dividing the product of k_a, the dissociation constant of the acid, and k_b, the dissociation constant of the base, by k_w, the dissociation constant of water. Since k_w has a fixed value and since either k_a or k_b can be made as great as one by using a strong acid or base for the standard solution employed, the equilibrium constant of such reactions is large in proportion as the dissociation constant of the acid or base being titrated is large.

A second series of processes of this group is based upon reactions involving the displacement of a weak acid or base from its salts by a strong acid or base. It has been shown on page 60 that the constant for such reactions can be calculated by dividing the dissociation constant of the strong acid or base used by the dissociation constant of the weak acid or base of which the salt is formed.

The End-Points of Processes Involving Neutralization. The true end-point of a titration in which a standard solution of a base is added to an acid corresponds to the point at which an equivalent

amount of the base has been added, that is, the point at which the ratio of the base added to the acid present equals 1. This ratio is less than 1 if an insufficient amount of base has been added, and exceeds 1 if an excess has been added. The concentration of the hydrogen ion in such mixtures depends upon the value of this ratio, the value of the equilibrium constant and the concentration of the solution. It can be calculated if all of these values are known.

Suppose, for example, we titrate 50 cc. of a 0.2 molar solution of an acid, whose dissociation constant is 10^{-2}, with a 0.2 molar solution of a strong base such as potassium hydroxide. The constant for the reaction which takes place has the value $1 \times 10^{-2} \div 10^{-14} = 10^{12}$. Let us calculate (H^+) after 48 cc. of base have been added.

The total concentration of base added is $0.2 \times \frac{48}{98} = 0.098$, that of the acid added is $0.2 \times \frac{50}{98} = 0.102$. Let x represent the fraction of the base which remains free and $(1 - x)$ the fraction which combines with the acid. Then $(0.098)\,x$ represents the concentration of base left uncombined and $0.098\,(1 - x)$ the concentration of base which combines with the acid; this is also the concentration of the acid which combines with the base and that of the salt formed. Then $0.102 - 0.098\,(1 - x)$ represents the concentration of the acid left uncombined. The law of mass action requires that

$$(HA) \cdot (KOH) \cdot K = (KA) \cdot (H_2O).$$

Making the proper substitutions and remembering that the concentration of water is practically constant, and can be disregarded, we obtain:

$$(0.098\,x)\,(0.102 - 0.098 + 0.098\,x)\,(10^{12}) = 0.098 - 0.098\,x,$$

or $$x^2 + 4.08 \times 10^{-2}\,x = 1.02 \times 10^{-11} - 1.02 \times 10^{-11}\,x,$$

from which $x = 3 \times 10^{-10}$, and $0.098\,x = 3 \times 10^{-11}$.

Since the dissociation of the base at this concentration is practically complete 3×10^{-11} also represents (HO^-) and hence (H^+) must have the value $10^{-14} \div 3 \times 10^{-11}$, or 3.3×10^{-4}.

In a similar manner the value of (H^+) after 49, 49.5, 49.7, 49.9, 50, 50.1, 50.3, 50.5 and 51 cc. have been added can be calculated. The results of these calculations are represented graphically in

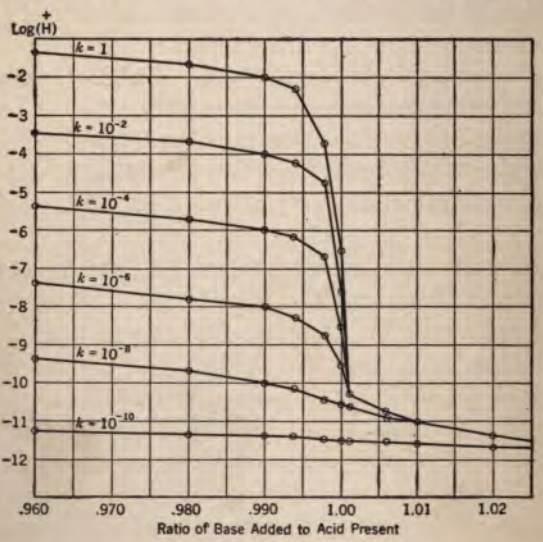

Fig. 56. — Curves Showing Changes in (H^+) in the Titration of Acids

the second of the series of curves of Fig. 56, in which the ordinates represent the common logarithms of (H^+) and the abscissas the ratio of base to acid present in the mixtures. It shows that the change in (H^+) associated with small changes in the value of this ratio is very much greater in the neighborhood of the point at which this ratio has the value one, than at those points at which it is slightly greater or less than one. The curve also shows that en this ratio has the value 1, (H^+) has the value 3.16×10^{-8} d of the value 10^{-7}, which it would have if the solution were

perfectly neutral. This is due to the fact that the dissociation constant of the acid is less than that of the base and therefore the hydrolysis of the salt formed yields a solution in which (H^+) is less than 1×10^{-7}.

If next we calculate a similar series of values for titrations in which acids having dissociation constants of 1, 10^{-4}, 10^{-6}, 10^{-8} and 10^{-10} are titrated with a strong base, and plot the results as before, we obtain the series of curves represented in the same figure. They show that the ratio of the change in (H^+) to the change in ratio of base to acid decreases as the dissociation constant of the acid decreases, even in the neighborhood of the point at which the ratio of base to acid is one. When the dissociation constant of the acid is 10^{-10} the curve shows no inflection at this point and the total change in (H^+) resulting from a very large change in the ratio of base to acid is extremely small. The curves also show that the value of (H^+) when this ratio is 1 differs from 10^{-7} in proportion as the dissociation constant of the acid is reduced.

If the method just used is employed to ascertain the changes in (HO^-) which take place when a series of bases are titrated with a strong acid, it will be found that the changes in (HO^-) resulting from a change in the ratio of acid to base have a maximum value in the neighborhood of the point at which the acid to base ratio is one, and are large in proportion as the dissociation constant of the base is large; also that the value of (HO^-) at the point of which this ratio is one differs from 10^{-7}, in proportion as the dissociation constant of the base is reduced.

The End-Points of Processes Involving Displacement. The value of (H^+) in a mixture obtained by adding a strong acid to a salt of a weak acid depends upon the ratio of the acid added to the salt present, the value of the equilibrium constant and the concentration of the solution; it can be calculated if these values are known.

Let us assume that a 0.2 molar solution of hydrochloric acid is added to 50 cc. of a 0.2 molar solution of the potassium salt of an

acid whose dissociation constant has the value 10^{-10}. Since the dissociation constant of hydrochloric acid can be represented by 1 the constant of the reaction is $1 \div 10^{-10}$, or 10^{10}.

Let us first calculate (H^+) after 48 cc. of strong acid have been added. The total concentration of this acid is $0.2 \times \frac{4}{5}\frac{8}{8} = 0.098$ and that of the potassium salt is $0.2 \times \frac{5}{5}\frac{0}{8}$, or 0.102. If x represents the fraction of hydrochloric acid left uncombined, $0.098\ x$ must represent the concentration left uncombined, $0.098\ (1 - x)$ the concentration of weak acid formed and $0.102 - 0.098\ (1 - x)$ the concentration of the potassium salt left uncombined. By making the proper substitutions in the expression representing the reaction we obtain

$$(0.098\,x)\ (0.102 - 0.098 + 0.098\,x)\ (10^{10}) = [0.098\ (1 - x)]^2.$$

When this expression is solved for x it is found to have the value 2.5×10^{-9} and $0.098\,x$ is 2.5×10^{-10}. The total value of (H^+) is the sum of that due to the dissociation of the hydrochloric acid, which is 2.5×10^{-10}, plus that due to the weak acid liberated. The total concentration of the weak acid liberated is $0.098\ (1 - x)$, which can be calculated to yield a concentration of hydrogen ion of 3.2×10^{-6}; hence the total value of (H^+) is 3.2×10^{-6}.

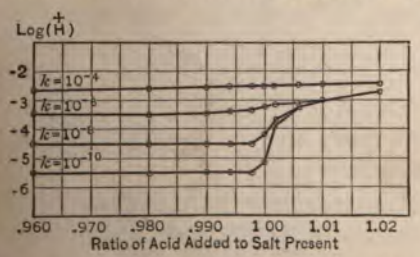

Fig. 57. — Curves Showing Changes in (H^+) in the Titration of Salts

The value of (H^+) after 49, 49.5, 49.7, 49.9, 50, 50.1, 50.3, 50.5, and 51 cc. of acid have been added can be calculated in a similar manner. The results of these calculations, also of similar calculations in which the dissociation constants of the liberated acids have the values 10^{-5}, 10^{-6} and 10^{-4}, are represented in the series of curves of Fig. 57 in which the ordinates represent the logarithms of (H^+) and the

abscissas the ratio of acid added to the salt present. They show that the rate at which (H^+) changes in the neighborhood of the true end-point, that is, where the ratio is 1, is large where $k = 10^{-10}$, is quite large where $k = 10^{-8}$, is very small where $k = 10^{-6}$, and is scarcely recognizable where $k = 10^{-4}$; also, that (H^+) at the true end-point is much greater than 10^{-7} even where $k = 10^{-10}$.

Methods Used for the Recognition of End-Points. The end-points of titrations which depend upon reactions involving either neutralization or displacement can be recognized by any device which indicates with sufficient accuracy the changes in (H^+) during the titration. The value of (H^+) can be measured directly by a method which involves the determination of the electromotive force between two hydrogen electrodes, one of which is placed in the solution being titrated, and the other in a solution containing known concentration of hydrogen ion.*

Advantage may also be taken of the fact that the rate of change in (H^+) is associated with a change in the conductivity of the mixture, and it is often possible to determine the true end-points by measuring the conductivity of the mixture during the titration. Both methods require the employment of elaborate and costly apparatus and have not been very largely used. The method commonly employed depends upon the use of certain organic reagents, which undergo pronounced color changes when (H^+) changes thru certain definite values.

Reactions of the Indicators Used. The indicators used for this class of processes are very weak acids or bases and form salts. The structural formulæ assigned to the salts of some of these indicators differ from those of the corresponding free acid or base, that is, the formation of salts is associated with a change in the position of one or more atoms in the molecule, and two "tautomeric" forms of the indicator must be assumed to exist. For example, the neutral and acidic solutions of the indicator phenol-

* Jour. of Am. Chem. Soc., **35** (1913).

phthalein, which is a very weak dibasic acid,* are colorless, but become deep red upon the addition of a small amount of base. It seems probable that the color of the solution is due to the presence of a divalent ion which contains the group $=C_6H_4=O$. This group is known to impart to solutions of compounds containing it a red color, and is known as a "chromophore." The free acid on the other hand does not contain this or any other chromophore, and for this reason neutral or acidic solutions of the indicator are colorless. The transformation of a colorless into a colored solution involves two separate processes. The first of these involves an equilibrium expressed by

$$(C_6H_4HO-C_8H_4O_2-C_6H_4HO)\ k_1 = (C_6H_4HO-C_8H_5O_2=C_6H_4=O)$$

The second involves the ionization of the indicator, which takes place in two stages and depends upon two sets of equilibria, namely:

$$(C_6H_4HO-C_8H_5O_2=C_6H_4=O)k_2=(C_6H_4HO-C_8\bar{H}_4O_2=C_6H_4=O)(\overset{+}{H})$$

and

$$(C_6H_4HO-C_8\bar{H}_4O_2=C_6H_4=O)k_3=(C_6H_4O-C_8\bar{H}_4O_2=C_6\bar{H}_4=O)(\overset{+}{H})$$

If we multiply the three equations together and simplify the resulting expression we obtain

$$k_1 \cdot k_2 \cdot k_3 \text{ or } K = \frac{(\overset{+}{H})^2\,(C_6\bar{H}_4O - C_8\bar{H}_4O_2 = C_6H_4 = O)}{(C_6H_4HO - C_8H_4O_2 - C_6H_4HO)}.$$

The value of K can be determined experimentally. If we compare the intensity of the color of a solution containing a known concentration of the indicator and of hydrogen ion, with the intensity of the color of a solution containing the same concentration of indicator in addition to sufficient base to change all of it into the chromophore-containing ion, we can determine the fraction of

* Jour. of Am. Chem. Soc., **34**, 1128 (1912).

indicator transformed into the colored form. If we represent this fraction by x the above expression becomes

$$K = \frac{(H^+)^2 x}{(1-x)},$$

from which the value of K can be calculated.

This expression can be used to determine the value of K for any dibasic indicator, whose color is due to the divalent ion only. The corresponding expression for any monobasic acid differs from it only in that (H^+) replaces $(H^+)^2$. The value of K is a numerical expression of the most important property* of this class of indicators, namely, their tendency to undergo a color change in the presence of a definite concentration of hydrogen ion. It is known as the "indicator constant" and will be referred to frequently in discussing the use of this class of indicators.

It has not been shown that all indicators of this class undergo a tautomeric transformation. If there are indicators of this class which do not undergo such changes the color change is due to dissociation alone, and the value of K must then equal the value of the dissociation constant of the indicator. If, however, the value of K is always ascertained by the method outlined, the theory of the cause of the color change is of no significance.

The Titration of Acids Using an Acidic Indicator. The general theory of indicators outlined in Chapter XXXV can be used in discussing these titrations. The factors which determine the completeness of the reactions concerned are the value of the indicator constant, and the dissociation constants of the acid and base used.

Let us assume that acetic acid ($k = 1.8 \times 10^{-5}$) is being titrated with potassium hydroxide ($k = 1$), and that para-nitro-phenol, which is a monobasic acid indicator whose constant has the value 10^{-7}, is used. If we disregard the tautomeric changes which this indicator may undergo the reactions concerned are expressed by

* Noyes, Jour. of Am. Chem. Soc., **32**, 815 (1910).

(1) $C_2H_3O(HO)+KOH \rightarrow C_2H_3O(KO)+H_2O,$

(2) $C_6H_4(NO_2)(HO)+KOH \rightarrow C_6H_4(NO_2)KO+H_2O,$

(3) $C_6H_4(NO_2)KO+C_2H_3O(HO) \rightarrow C_6H_4(NO_2)HO+C_2H_3O(KO).$

Since acidic solutions of the indicator are colorless while basic solutions are yellow the appearance of the end-point here depends upon the concentration of the $C_6H_4NO_2O$ ion, and the process corresponds to the first of the two classes discussed in Chapter XXXV.

The value of K for (1) is $1 \times 1.8 \times 10^{-5} \div 10^{-14} = 1.8 \times 10^{9}$.

The value of K for (2) is $1 \times 10^{-7} \div 10^{-14} = 10^{7}$.

The value of K for (3) is $1.8 \times 10^{-5} \div 10^{-7} = 1.8 \times 10^{2}$.

The values of K for (1) and (2) are sufficiently large, that for (3) is too small, that is, this reaction is sufficiently reversible to make it probable that a recognizable amount of the chromophore-containing ion may be formed before all of the acetic acid is neutralized. If a more weakly acidic indicator, such as one for which $k = 10^{-10}$ is used, K for (2) would have the value 10^{4} and for (3) 1.8×10^{5}. In this case there is greater danger of an error from the reversibility of (2) than of (3), that is, it might be necessary to
an appreciable excess of the titrating solution to produce a
able amount of the chromophore-containing ion. The
cator which could be used would have a constant of
$^{-10}$ since K for both (2) and (3) would then have the
$\times 10^{4}$.

scussion makes it clear that in the titration of acids with
indicator the constant of the indicator used must be
ompared with the dissociation constant of water, but
ompared with the dissociation constant of the acid being
further, if an indicator whose constant has a certain
ised, the probability of obtaining a deferred end-point
and and of a premature end-point on the other is equal.

on of Bases with Acidic Indicators. Let us assume
a hydroxide ($k = 1.8 \times 10^{-5}$) is titrated with hydro-

chloric acid ($k = 1$) and that para-nitro-phenol is again used as the indicator. This titration corresponds to the second of the two cases discussed in Chapter XXXV. The reactions concerned are

(4) $(NH_4)HO + C_6H_4(NO_2)HO \rightarrow C_6H_4(NO_2)(NH_4)O + H_2O$,
(5) $(NH_4)HO + HCl \rightarrow (NH_4)Cl + H_2O$,
(6) $C_6H_4(NO_2)(NH_4)O + HCl \rightarrow C_6H_4(NO_2)HO + (NH_4)Cl$.

The end-point here recognized is that at which the concentration of the chromophore-containing ion changes from a recognizable quantity to one which cannot be recognized with certainty.

The value of K for (4) is $(10^{-7})\ (1.8 \times 10^{-5}) \div 10^{-14}$, or 1.8×10^{2}.
The value of K for (5) is $(1.8 \times 10^{-5})\ (1) \div 10^{-14}$, or 1.8×10^{9}.
The value of K for (6) is $1 \div (10^{-7})$, or 10^{7}.

The values of K for (5) and (6) are sufficiently large, that for (4) is too small to insure the presence of a recognizable concentration of the chromophore-containing ion up to the point at which all of the base has been neutralized. The best indicator which could be used would have a constant of 2.4×10^{-5}, for with such an indicator the value of K for both (4) and (6) would be 4.2×10^{4}.

It is evident that in the titration of bases with acidic indicators the indicator constant should be large in proportion as the dissociation constant of the base being titrated is small, but must be small as compared with the dissociation constant of the acid used for the titration; further, if an indicator whose constant has a certain value is used the probability of obtaining a deferred end-point on the one hand and a premature end-point on the other is equal.

The Use of Basic Indicators. The indicator constant of a basic indicator could be defined by an expression analogous to that used for acidic indicators, that is, by

in which Q^- represents the chromophore-containing ion. Since in any aqueous solution $(H^+) \cdot (HO^-) = 10^{-14}$ we can substitute $10^{-14} \div (H^+)$ for (HO^-) and obtain an expression for K in terms of (H^+) and the fraction of indicator transformed. There is no objection to substituting (H^+) for $10^{-14} \div (H^+)$ and changing the value of K to correspond with the effect of this substitution, that is to define the indicator constant of basic indicators the same as for acidic indicators. There is further no difficulty in determining the value of this constant in such a manner as to conform to this definition. It is only necessary to use a large excess of acid instead of base to completely transform the indicator in the solution used as a standard of comparison in order to obtain x, and from it and the known value of (H^+) to calculate K. It should be noted, however, that altho the constant of an acidic indicator varies directly with its dissociation constant, that of a basic indicator varies inversely with its dissociation constant, and hence strongly acidic and weakly basic indicators show similar properties.

By the use of this general definition it becomes unnecessary to distinguish between acidic and basic indicators, and the rules elaborated in the preceding discussion are valid for both classes of indicators.

The Sensitiveness of Indicators. In the preceding discussion it is shown how the value of the indicator constant K can be calculated after having determined the value of (H^+) at which the color change corresponding to the transformation of a particular fraction (x) of the total amount of indicator present takes place. It might be surmised that the color change referred to is always that at which the concentrations of the two modifications of the indicator are the same, since such mixtures should yield what might be called the "neutral color" of the indicator in question. Incidentally it should be pointed out that if this condition is complied with, that is, if the fraction transformed is represented by 0.5, the fraction $x \div (1 - x)$ equals one, and

therefore $K = (H^+)$; that is, the value of the indicator constant must equal the concentration of the hydrogen ion at which the color change representing the transformation of one-half the total amount of indicator present, takes place.

It is found, however, that the color changes which many indicators undergo when $x = 0.5$ is less clearly defined than when x has a greater or less value. This is due to the fact that the eye is less sensitive to certain colors than others and is often unable to correctly interpret the composition of mixtures. The colors of some indicators, however, change with varying (H^+) at a fairly uniform rate, and any shade of the series can be adopted as the end-point with about equal advantage. Decided differences are also apparent in the total change in the value of (H^+) within which any easily recognizable color change takes place, that is, the "sensitiveness" of the different indicators varies greatly. In general, two-color indicators, that is, those which change from one distinctive color to another, are less sensitive than one-color indicators, which change from one distinctive color to a colorless form or the reverse.

Before an indicator can be used intelligently certain facts regarding it should be ascertained. First, the particular color change which can be recognized most accurately should be decided upon and always used as the correct end-point. Second, the value of (H^+), at which this change takes place, should be determined by noting the effect of adding it to a series of solutions containing varying concentrations of the hydrogen ion. Third, the fraction transformed at the value of (H^+) found should be determined, and finally the value of K calculated. With indicators which show a continuous series of color changes, several different shades may be chosen as end-points and hence different values for (H^+) found.

Classification of Indicators. The uses of the different indicators are shown most advantageously by arranging them in a series with respect to the value of (H^+) between which they show

the most pronounced color changes. At one end of the series will be found the indicator whose constant has the largest permissible value, and which is peculiarly adapted to the determination of weak bases; at the other end, the one whose constant has the smallest permissible value, and which is peculiarly adapted to the determination of weak acids. Each member of the series can be used for the determination of acids and bases whose dissociation constants vary between certain values with a fair degree of accuracy. Where greater accuracy is demanded it is necessary to make use of different concentrations and adopt different color changes for the same indicator in order to limit still further the range of concentrations of (H^+), which can be easily recognized.

A series of five indicators arranged in the order of increasing sensitiveness toward (H^+) is given in the following paragraphs.

Methyl Orange. This indicator is the sulfonate of dimethylaniline-azobenzene; altho the imino group gives it weakly basic properties, its use as an indicator probably depends upon the strongly acidic sulfonic acid group. It is used in the form of a solution which contains 1 gm. per liter of its sodium salt. When the volume of solution being titrated does not exceed 100 cc. one drop of this solution imparts an easily recognizable yellow color, which is not changed by the addition of a base, to the mixture. If sufficient acid is added to make (H^+) equal to 10^{-4} the solution becomes pink. A series of intermediate transition colors begins to appear when $(H^+) = 10^{-5}$. The most clearly defined color change is obtained when the minimum concentration is used and at least 80 per cent of the indicator is transformed. The value of its constant is 5×10^{-4}. This is the most strongly acidic indicator in general use. It is especially useful in the titration of very weak bases; the weaker acids, such as carbonic, boric, hydrocyanic, have almost no effect upon it, altho large concentrations delay somewhat the speed with which it responds to changes in (H^+).

Cochineal. This indicator is usually prepared by digesting the dried cochineal insects with ten parts of 50 per cent alcohol and filtering. The resulting tincture owes its color to carminic acid the structural formula of which is not known. With pure water it yields a ruby red color which changes to violet red upon the addition of a base and to yellow upon the addition of an acid. The most decided color change takes place when (H^+) is in the neighborhood of 1×10^{-5}. It is therefore slightly more sensitive toward weak acids and less toward weak bases than methyl orange.

Para-nitro-phenol. This indicator is used as an aqueous solution containing 4 gm. per liter. One drop is sufficient for titrations in which the total volume does not exceed 100 cc. Its constant has the value 1×10^{-7} when 20 per cent of it is transformed. The change from colorless to greenish-yellow takes place when (H^+) changes from 10^{-5} to 10^{-6}.

Rosolic Acid. This is the anhydride of trioxy-triphenyl-carbinol. It is usually employed in the form of an alcoholic solution which contains two-tenths of 1 per cent. One drop of this solution imparts to 100 cc. of water a light yellow color, which is not changed by the addition of acids but becomes violet red when (H^+) is reduced to 10^{-8}. Its constant has the value 10^{-8} when the indicator is 20 per cent transformed.

Phenolphthalein. This indicator is prepared by dissolving 2 gm. in a liter of 50 per cent alcohol. One drop is sufficient for 100 cc. of solution. It imparts no color to pure water, but the solution changes to deep red when (H^+) is changed from 10^{-8} to 10^{-10}. Its constant has the value 1.7×10^{-10} when 20 per cent of it is transformed.

CHAPTER XLI

APPLICATIONS OF THE METHODS OF ACIDIMETRY AND ALKALIMETRY

I. Determination of Acids and Acid Salts

Titration of Monobasic Acids. In determining an acid by titrating with a strong base the general principles developed on pages 286 and 287 can be used to ascertain the proper indicator to employ, or that indicator can be chosen from the series which gives a color change at that value of $(\overset{+}{H})$, which the solution should have at the true end-point. This value can be inferred with sufficient accuracy from the data given on the curves of Fig. 56, at least for the concentrations there made use of, but it is sometimes advantageous to estimate $(\overset{+}{H})$ by calculating to what extent the reaction concerned takes place in the reverse direction. At the true end-point the solution must in every case have the same composition as one obtained by adding the proper amount of the salt formed to pure water, therefore we can calculate the value of $(\overset{+}{H})$ in such solutions from the hydrolysis constant (see page 59) of the salt formed, or we can ascertain this point empirically, that is, by finding which indicator of the series shows a color change when $(\overset{+}{H})$ is changed very slightly from the value it has in a solution made by adding the salt to pure water.

In titrating hydrochloric acid, for instance, the solution at the true end-point should contain the same concentration of $(\overset{+}{H})$ and $(H\overset{-}{O})$ as one prepared by adding pure sodium chloride to water, and if the dissociation of both acid and base be considered both $(\overset{+}{H})$ and $(H\overset{-}{O})$ must have the value 1×10^{-7}.

It might be inferred that in the titration of all strong acids the indicator rosolic acid, which gives a color change when $(\overset{+}{H})$ equals 1×10^{-7}, should be used, but satisfactory results can also be obtained with any indicator of the series. The reason is that in titrating any strong acid the addition of a single drop of a solution of the standard alkali in the neighborhood of the true end-point changes $(\overset{+}{H})$ thru differences as great as those represented by the two extremes of the indicator series, that is, where the solution used is at least tenth-normal and the volume titrated is not too large. In the titration of the weaker acids greater care must be used in the choice of an indicator, but this does not necessarily insure a high degree of accuracy. This depends in large measure upon the sensitiveness of the indicator and still more upon the rate at which $(\overset{+}{H})$ changes during the titration in the neighborhood of the true end-point.

Titration of Di- and Tribasic Acids. The theory of the titration of these acids is more complex since they dissociate in stages and each stage of the process is characterized by a definite dissociation constant. For example the dissociation of phosphoric acid is represented by

$$(1) \qquad (\overset{+}{H})(H_2\overset{-}{P}O_4) \div (H_3PO_4) = k_1 = 1 \times 10^{-2},$$

$$(2) \qquad (\overset{+}{H})(\overset{--}{H}PO_4) \div (H_2\overset{-}{P}O_4) = k_2 = 2 \times 10^{-7},$$

$$(3) \qquad (\overset{+}{H})(\overset{---}{P}O_4) \div (\overset{--}{H}PO_4) = k_3 = 4 \times 10^{-13}.$$

When this acid is titrated with a base three different equilibrium constants, whose values depend upon the three dissociation constants, have to be considered. The value of $(\overset{+}{H})$ during the titration is determined for the most part by k_1 up to the point at which one equivalent of base has been added, by k_2 up to the point at which two equivalents of base have been added, and by k_3 up to the point at which three equivalents of base have been added. If a curve similar to those of Fig. 56 is plotted it will be found that

those portions of it which are in the immediate neighborhood of the points at which exactly one and two equivalents of base have been added are nearly vertical, that is, at these points $(\overset{+}{H})$ changes very decidedly with slight changes in the value of the ratio of base to acid. Experience shows that the value of $(\overset{+}{H})$ at the first of these points corresponds approximately to the value at which the color of methyl orange changes; at the second point it corresponds to the value at which the color of phenolphthalein changes. Hence this acid can be determined by using methyl orange and assuming that it is monobasic, or by using phenolphthalein and assuming that it is dibasic. In neither case are the end-points very sharply defined and the method yields approximate results only. The proper conditions for the titration of all di- and tribasic acids can be indicated if the dissociation constants of these acids are known.

Dissociation Constants of Acids. The dissociation constants of some of the acids which the chemist is frequently required to determine are given in the table on page 295.

Titration of Acid Salts. When an acid salt of a strong base, such as NaH_2PO_4, is dissolved in water the value of $(\overset{+}{H})$ in the resulting solution is determined for the most part by one of the dissociation constants of the acid concerned, in the illustration cited by k_2 of phosphoric acid. If such solutions are titrated with a base it is often possible to recognize the point at which exactly one equivalent of base has been added, owing to the very great change in the value of $(\overset{+}{H})$ at this point. In the solution of NaH_2PO_4 the point at which one equivalent of base has been added can be recognized by the use of phenolphthalein, and the process is identical with that part of the titration of phosphoric acid in which $(\overset{+}{H})$ changes from the first to the second of the two points at which it changes abruptly. The method is only appli- the titration of acid salts of strong bases and a limited li- and tribasic acids.

DISSOCIATION CONSTANTS OF ACIDS *

Name of acid	Formula	First stage	Second stage
.....	$H(C_2H_3O_2)$	1.8×10^{-5}	.....
ic.....	H_3AsO_4	5×10^{-3}	.....
ious.....	H_3AsO_3	6×10^{-10}	.....
.....	H_3BO_3	7×10^{-10}	.....
nic.....	H_2CO_3	3×10^{-7}	3×10^{-11}
ous.....	HClO	4×10^{-8}	.....
ic.....	$HClO_3$	<1	.....
nic.....	H_2CrO_4	<1	6×10^{-7}
.....	$C_3H_4(HO)(COOH)_3$	8×10^{-4}	.....
c.....	H(COOH)	2.14×10^{-4}	.....
chloric.....	HCl	<1	.....
cyanic.....	HCN	1.3×10^{-9}	.....
bromic.....	HBr	<1	.....
odic.....	HI	<1	.....
sulfurous	H_2S	9×10^{-8}	1×10^{-15}
us.....	HNO_2	5×10^{-4}	.....
.....	HNO_3	<1	.....
.....	$(COOH)_2$	3.8×10^{-2}	5×10^{-5}
loric.....	$HClO_4$	<1	.....
horic.....	H_3PO_4	1.1×10^{-2}	2×10^{-7}
ic.....	H_2SO_4	<1	3×10^{-2}
ilic.....	$C_2H_4(COOH)_2$	6.6×10^{-5}	.....
ric.....	$C_2H_2(HO)_2(COOH)_2$	9.7×10^{-4}	.....

st of the data here presented is from the table compiled by Noyes, Jour. of Am. Chem. , 860 (1910). Some values are from Ostwald, Zeit. für Phys. Chemie, **3**, 418 (1889), or from r, Jour. of Am. Chem. Soc., **30**, 713 (1908).

II. Determination of Bases and Basic Salts

ration of Bases. The theory of the titration of bases is gous to that of the titration of acids, but unfortunately the iation constants of bases have not been determined except ew instances. The dissociation constants of all the alkaline xides are large and at moderate concentrations can be rep- ted approximately by one. The hydroxides of the alkaline s are but slightly soluble, and readily change into oxides; are all dibasic and probably dissociate in stages. The hy- les and oxides of the remaining metals are so insoluble that

they have no appreciable effect on the color of a solution of methyl orange. Some of them, such as ZnO, can be determined by the method of back titration, that is, by adding a measured volume of standard acid more than sufficient to react with the base, and titrating the excess of acid used with a standard base.

The dissociation constant of ammonium hydroxide has the value 1.8×10^{-5} and it can be accurately titrated if methyl orange or cochineal is used. Some of the substituted ammonias, except those of the aromatic group, are still stronger bases. A limited number of alkaloids possess basic properties strong enough to make it possible to titrate them directly with a fair degree of accuracy.

Titration of Basic Salts. Many of the basic salts which have been described are mixtures and the composition of many others is not known accurately. Where the formulæ of a basic salt is known it can frequently be determined by methods exactly analogous to those used for the determination of acid salts.

III. Determination of Salts of Weak Acids and Bases

Titration of Salts of a Weak Acid with a Strong Acid. The data represented by the curves of Fig. 57 show that when salts of acids, whose dissociation constants are not greater than 1×10^{-9}, are titrated with a strong acid, both the rate at which $(\overset{+}{H})$ changes and the absolute value of $(\overset{+}{H})$ at the true end-point is such as to make recognition of this end-point, by the use of such an indicator as methyl orange, possible. At the true end-point the solution must have the same composition as one obtained by adding the proper amount of the new salt formed and the acid liberated to pure water. If the dissociation constant of the base equals that of the strong acid added, the salt formed has only a slight effect upon $(\overset{+}{H})$; its value depends almost entirely upon the dissociation constant of the liberated acid and its concentration. If, for example, we titrate sodium borate

with hydrochloric acid, the value of $(\overset{+}{H})$ at the true end-point is very nearly equal to that of the boric acid liberated.

When the acid of which the salt is composed is di- or tribasic an indicator can be used which will determine the point at which either one, two or three equivalents of the stronger acid have been added. In the titration of sodium carbonate for example the method might be based upon one of two reactions, namely,

(1) $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl,$

(2) $Na_2CO_3 + 2\,HCl \rightarrow CO_2 + H_2O + 2\,NaCl.$

If the former method is used the value of $(\overset{+}{H})$ at the true end-point would equal that resulting from the dissociation of $\overset{-}{HCO_3}$ at the concentration concerned. If the latter method is used the value of $(\overset{+}{H})$ at the true end-point would equal that resulting from the dissociation of H_2CO_3 at the concentration concerned, but since H_2CO_3 breaks down into CO_2 and H_2O this concentration is very small. Experience shows that the latter method is much more accurate than the former.

Titration of Salts of a Weak Base with a Strong Base. The theory of the titration of salts which represent combinations of very weak bases and strong acids is entirely analogous to that of the processes discussed in the preceding section. They are used for the titration of salts of the aromatic amines and alkaloids.

IV. Indirect Determinations

Titrations Which Involve a Previous Separation. A large number of substances which cannot be determined directly by titrating with an acid or base may be transformed into substances which can be so determined. This includes a large number of the metallic elements which form insoluble salts with weak acids. Thus, altho calcium when present as a salt cannot be titrated directly, it can be precipitated from its solutions as a carbonate, filtered and washed, and then titrated like any other salt which

represents a combination of a weak acid and a strong base. The accuracy of the process depends upon the insolubility of the precipitate, upon the completeness with which the precipitating agent, in this case ammonium carbonate, can be washed out, and upon the accuracy of the final titration.

Another illustration is found in a method which is largely used for the determination of phosphoric acid when in the form of its salts. It is based upon the fact that this acid is, under proper conditions, completely precipitated by ammonium molybdate as $(NH_4)_3PO_4 \cdot 12\,MoO_3$ which compound reacts with a solution of sodium hydroxide as shown by the expression:

$$2\,(NH_4)_3PO_4 \cdot 12\,MoO_3 + 46\,NaHO \rightarrow 2\,(NH_4)_2HPO_4 + 23\,Na_2MoO_4 + (NH_4)_2MoO_4 + 22\,H_2O.$$

As this reaction is practically complete and instantaneous we can titrate the MoO_3 combined with the ammonium phosphate, and the amount of phosphorus present can be calculated from the assumption that every twelve molecules of MoO_3 found represent one molecule of phosphoric acid originally present.

Titrations Which Involve the Use of a Special Reagent to Increase Dissociation. In a limited number of instances the desired transformation can be effected by the use of a reagent which does not itself react with the titrating solution, and in such determinations previous separation of the product is not necessary. Thus hydrocyanic acid, whose acidic properties are too weak to admit of a direct titration, can be completely changed into mercuric cyanide and hydrochloric acid by the addition of mercuric chloride, and the resulting hydrochloric acid can be titrated with accuracy. The process owes its accuracy to the remarkably low dissociation constant of mercuric cyanide.

V. Questions and Problems. Series 20

1. Calculate $(\overset{+}{H})$ and $(\overset{-}{HO})$ in solutions made by adding to 100 cc. of water (a) 1 gm. of 80 per cent $(C_2H_3O_2)H$, (b) 1 cc. of concentrated hydrochloric acid, assuming that both acids obey the dilution law. (See page 54.)

2. Indicate the probable form of the curves representing the changes in $(\overset{+}{H})$ during the titration of H_3PO_4, assuming that three equivalents of base are used.

3. Calculate $(\overset{+}{H})$ and $(\overset{-}{HO})$ at the true end-point when a normal solution of an acid is titrated with a normal solution of a base if the dissociation constant of both acid and base is 1×10^{-4}.

4. What indicator would you use in titrating acetic acid with ammonium hydroxide? Why is it preferable to titrate with sodium hydroxide?

5. What is the simplest method of ascertaining experimentally whether sodium benzoate can be titrated with HCl with accuracy?

6. An indicator which imparts no color to an acid solution gives a particular shade of yellow to a solution in which its concentration is 6×10^{-5} and $(\overset{+}{H})$ equals 0.81×10^{-9}; it is found that a layer of this solution 25 cm. thick, which contains the same concentration of indicator, has the same color absorption as one 10 cm. thick, which contains the same concentration of indicator and an excess of base; what is the value of the indicator constant?

Ans. 5.4×10^{-10}.

7. If the indicator constant of cyanin has the value 2×10^{-9} when considered an acid indicator, what is the corresponding value when considered a basic indicator? *Ans.* 5×10^{-6}.

8. Would you think it possible to determine the following acid salts by a direct titration with a base; $NaHSO_4$, $NaHCO_3$, $HCOOKCOO$, Na_2HPO_4?

9. Would you think it possible to determine the following salts by titrating with an acid $Na(C_2H_3O_2)$, $(NH_4)_2CO_3$, K_2SO_3, Na_3PO_4, $CaCrO_4$?

10. If required to determine the percentage of H_3PO_4 by the method outlined on page 298, what value would you give to E of the general formula in calculating the result?

CHAPTER XLII

THE PREPARATION OF STANDARD SOLUTIONS OF ACIDS AND BASES

I. Factors to be Considered

Choice of the Acid and Base. As noted in Chapter XL it is essential that the acids and bases used for the preparation of standard solutions have large dissociation constants. It is also desirable that they shall be stable compounds, that their action on the glass vessels used to retain them be small, and that they exercise no oxidizing or reducing action on the indicators used. These considerations limit the acids generally used to hydrochloric and sulfuric. For bases the hydroxides of sodium and potassium are most frequently employed, but the hydroxides of ammonium and barium are sometimes used.

The Most Desirable Strength. Every titration should require the use of a moderately large volume of the standard solution; hence in titrating substances of low percentage composition either a large amount of sample must be used or the concentration of the solution used must be small. On the other hand, strong solutions give more decisive end-points than weaker solutions and their strength is changed to a less extent relatively by carbon dioxide which may be absorbed from the air. In general it is not desirable to use solutions of acids or bases stronger than one-half, or weaker than one-tenth normal, altho special circumstances may make it desirable to vary these limits.

Methods of Preparing Solutions. Since the concentration of moderately strong sulfuric acid (preferably about 60 per cent) can be determined with very great accuracy from its specific gravity

(see Chapter XLIX) a standard solution of this acid can be prepared by diluting a weighed amount to the calculated volume. Similarly a standard solution of hydrochloric acid can be prepared by passing pure dry hydrochloric acid gas into a flask containing a weighed amount of water, determining the increase in the weight of the flask and diluting the solution to the calculated volume.

An indirect method in which a solution of approximately the desired strength is first prepared, its strength accurately determined by an independent process, and then diluted to the calculated volume is often preferable. The exact value of the diluted solution can be determined by a gravimetric process or by titrating against a known weight of some pure substance with which the solution reacts completely. A large number of such substances have been proposed and are used by different chemists for this purpose.

Sodium carbonate can usually be obtained sufficiently pure, except for small amounts of water and bicarbonate; if heated to 300° in a platinum crucible for a few minutes it gives the pure normal carbonate which can be weighed accurately and titrated against solutions of mineral acids using methyl orange as the indicator.

Calcium carbonate which has been separated by precipitation is also to be had in a very high degree of purity, and can be used like the sodium compound.

Borax ($Na_2B_4O_7 \cdot 10\ H_2O$) is readily obtained pure by recrystallization at temperatures below 50° and also gives accurate results in the standardization of acids.

Succinic and benzoic acids can also be prepared in a high degree of purity and simple and accurate methods for the standardization of alkaline solutions are based upon their use.

II. Outline of Method for the Preparation of Semi-normal Acid and Alkali

Preparation of Solutions. Weigh out on a rough balance 50 gm. of pure sodium hydroxide, place in a 2500 cc. flask, add 2 liters of distilled water and shake occasionally until the alkali is completely dissolved. Next add about 5 gm. of finely powdered C. P. calcium oxide and allow the mixture to stand for an hour with occasional shaking, or still better allow it to stand over night. Place a Witt filter-plate in a filtering tube and provide with a good thickness of washed asbestos in the customary manner; connect the filter tube with a clean two-liter bottle as shown in Fig. 58 and filter the alkali solution into the bottle. Keep the bottle stoppered as far as possible.

Fig. 58. — Device for Filtering Alkali Solution

Measure out 100 cc. of concentrated C. P. hydrochloric acid into a clean two-liter bottle, dilute to 2 liters with water which is free from carbon dioxide and mix thoroughly. To determine whether the carbon dioxide is present in objectionable amounts add one drop of phenolphthalein indicator to 200 cc. of the water in question, and then one drop of the approximately semi-normal alkali solution; if the mixture does not acquire a distinct pink color the amount of carbon dioxide is excessive, and the water must be heated to the boiling point to remove it.

Determination of the Volumetric Ratio. Measure out a 25 cc. pipet full of the acid solution into a 200 cc. beaker or Erlenmeyer flask, dilute to 50 cc. and add a drop of methyl orange indicator. Place a piece of white paper under the vessel and then add the alkali solution from a buret until the mixture, after passing thru a series of color shades, finally changes permanently to a clear lemon yellow. The color shade finally obtained should correspond to

that which results from the addition of one drop of the indicator to 75 cc. of water. Repeat this determination until the results of successive determinations do not differ by more than one part in five hundred. From the average of the results finally accepted, that is, those which are believed to involve no large errors, calculate the volumetric ratio of the two solutions by dividing the volume of alkali solution used by the volume of acid solution used.

Titration Against Pure Calcium Carbonate. Weigh out 0.8 gm. of pure and recently dried calcium carbonate into a 300 cc. beaker, cover with a watch glass and introduce 50 cc. of the acid solution measured preferably from a pipet. Agitate the contents of the beaker until the carbonate is completely dissolved, then warm gently to a temperature not exceeding 60° for the purpose of expelling the large excess of carbon dioxide. Rinse off the under side of the watch glass and the sides of the beaker with 25 cc. of water, add a drop of methyl orange indicator and titrate as in the determination of the volumetric ratio.

Calculation of Strength of the Two Solutions. Calculate the volume of acid solution equivalent to the volume of alkali solution used in the last titration by dividing by the volumetric ratio, and subtract the quotient from the 50 cc. of acid solution used. Calculate the weight of hydrochloric acid theoretically required to react with the calcium carbonate weighed out, and divide by the volume of acid solution found to be equivalent to it in the previous calculation; the quotient represents the weight of hydrochloric acid present in 1 cc. of the solution. Repeat the standardization with a second portion of calcium carbonate or until results are obtained which do not differ by more than one part in 500.

Calculate the weight of sodium hydroxide needed to neutralize the hydrochloric acid in 1 cc. of the solution of that reagent as originally prepared and divide by the volumetric ratio; the quotient represents the weight of sodium hydroxide present in 1 cc. of the alkali solution.

Reduction to Semi-normal Strength. Calculate the volume to which 1500 cc. or some other convenient volume, of the solution should be diluted to make each cubic centimeter contain exactly 0.01823 gm. and add the necessary amount of water, assuming that neither contraction nor expansion takes place. In making this dilution first rinse out a 1000 cc. and a 500 cc. flask with a little of the acid solution and discard; then fill the flasks to the mark with the solution and discard whatever remains in the bottle, but do not rinse the latter with water; next drain the contents of the two flasks into the bottle and add the calculated amount of water which should be measured accurately from a buret.

Dilute in a similar manner the alkali solution to semi-normal strength, that is, so that each cubic centimeter contains exactly 0.020 gm.

Checking Work. Redetermine the volumetric ratio between the two solutions; if it differs from one by more than two parts in one thousand faulty work has been done and, since the error may be in either one or both of the two solutions, the standardization with pure calcium carbonate must then be repeated. If difficulty is experienced in attaining the requisite accuracy by this method standardize the acid solution by the gravimetric method described below. If either of the solutions has been diluted to below semi-normal strength it is not necessary to prepare a new solution, but the exact factor representing the relation of the solution to normal strength should be calculated and used in place of the factor one-half wherever this factor would have been used.

Gravimetric Method of Standardization. Remove with a pipet 25 cc. of the acid solution, dilute to 200 cc. and add a slight excess, that is, about 10 per cent more silver nitrate than is theoretically required to react with the chlorine present. Heat the mixture to boiling and stir until the precipitate coagulates, then filter on an asbestos filter, wash dry and weigh resulting silver chloride. Calculate the relation of the acid solution to normal strength from the weight of silver chloride obtained from each

cubic centimeter of acid measured out. Calculate the relation of the alkali solution to normal strength from the volumetric ratio and the normal value of the acid solution.

III. Experiments With Indicators

Prepare one-tenth normal solutions of acid and alkali by diluting 50 cc. portions of the semi-normal solutions already prepared to exactly 250 cc. Remove by means of a pipet 10 cc. of the one-tenth normal acid solution to a 200 cc. beaker or Erlenmeyer flask, add 80 cc. of water, a drop of methyl orange indicator and titrate with the tenth normal alkali. Note and record all of the shades of color thru which the solution passes, the color when an equivalent amount of alkali has been added, the amount of alkali needed to bring about the most pronounced color change and the color when an excess of alkali has been added. Next pass a stream of carbon dioxide, which has been washed free from other acids, thru the solution and note the effect, if any, on the color of the solution.

Perform a similar series of experiments with the indicators, cochineal, rosolic acid, para-nitro-phenol and phenolphthalein.

IV. Questions and Problems. Series 20

1. If the water used in preparing the standard acid had been saturated with carbon dioxide, how and under what conditions would it have affected the results obtained with this solution?

2. If the calcium carbonate used had contained one per cent of calcium oxide, how would the results obtained with the standard acid and standard base be affected?

3. A solution of sulfuric acid is prepared by weighing out 5 gm. of pure $CuSO_4 \cdot 5\,H_2O$, dissolving in water, and precipitating the copper by electrolysis; if this solution is diluted to 1000 cc., what relation does it bear to normal?

4. Calculate by the simplest method the normality of solutions of sodium hydroxide one cc. of which react with (a) 0.02 gm. of benzoic acid, $C_6H_5(COOH)$; (b) 0.04 gm. of succinic acid, $(CH_2)_2(COOH)_2$; 0.015 gm. of crystallized oxalic acid, $C_2H_2O_4 \cdot 2\,H_2O$.

CHAPTER XLIII

DETERMINATIONS WITH A STANDARD ACID AND A STANDARD BASE

I. Determination of the Strength of Concentrated Sulfuric Acid

Outline of the Method. Weigh accurately a clean glass-stoppered weighing bottle of about 10 cc. capacity. Prepare a clean and dry dropping-tube or pipet of about 3 cc. capacity; insert into the bottle containing the sample and fill about half full. Remove from the bottle and allow about 15 drops to flow into the weighing bottle, being very careful to avoid spattering, then close the bottle and weigh accurately. Fill the bottle nearly full of water, mix and pour into a 200 cc. beaker, then rinse out at least three times with 10 cc. portions of water. Add a drop of any desired indicator and titrate with the standard alkali solution. Calculate the percentage of H_2SO_4 by the use of the general formula.

II. Determination of the Acidity of Vinegar

Preliminary Statements. The acidity of vinegar, unless adulterated with sulfuric acid, is due almost entirely to acetic acid. When titrated with a base the coloring matter present undergoes a gradual color change which is difficult to characterize; this change can be distinguished with fair accuracy from the color change of phenolphthalein if a large amount of the indicator is added and the solution diluted sufficiently. In extreme cases, that is, where the color is very intense, it may be necessary to remove it by the addition of bone black and filtering, but since this reagent absorbs small amounts of acid its use should if

possible be avoided. It is customary to report results in terms of the total weight of acid, calculated as acetic, per cubic centimeter of sample.

Outline of Method. Measure out 10 cc. of the vinegar into a 400 cc. beaker and dilute with 200 cc. of water free from carbon dioxide. Add three drops of phenolphthalein and titrate with the alkali solution, disregarding the changes from brown to drab and endeavoring to recognize the point at which the pink of the phenolphthalein, modified to some extent by the drab color of the vinegar, becomes apparent. Calculate the weight of acetic acid in 1 cc. of sample.

III. Determination of Potassium Bitartrate in Argol or Commercial Cream of Tartar

Preliminary Statements. The chief source of cream of tartar and tartaric acid is the argol which separates on the sides of the casks during the manufacture of wine. It contains in addition to potassium bitartrate ($C_4H_5KO_6$) salts of a number of organic acids and large amounts of coloring matter. The dissociation constant of the first hydrogen atom of tartaric acid is 9.7×10^{-4}, that of the second has not been accurately determined but it is sufficiently large to justify regarding it as a dibasic acid when titrated with a base if phenolphthalein is used as the indicator and therefore potassium bitartrate is one of the acid salts which can be titrated directly.

The large amount of coloring matter present in argol often makes it difficult to recognize the true end-point; the conditions observed in the titration of vinegar also apply here.

Outline of the Method. Weigh out 2 gm. of the finely powdered sample, add 150 cc. of hot water and stir for a few minutes. If a large amount of insoluble matter remains, filter on a small filter and wash with hot water until the washings are free from acidity. Add three drops of phenolphthalein and titrate with the standard alkali solution. Calculate the percentage of potassium bitartrate.

IV. Determination of Boric Anhydride in Natural Borates

Theory of the Method. The naturally occurring borates, which include the minerals colemanite, ulexite and pandermite, are simple or double borates of calcium and sodium. They are usually associated with the carbonates and sulfates of the alkali metals and with clay and sand. As they are the source of most of the borax and boric acid of commerce the value of ores containing them depends upon the percentage of boric anhydride which they contain.

The dissociation constant of boric acid is so small that it is completely displaced from solutions of its salts by an equivalent amount of a strong acid; if the salts are insoluble an excess of the acid must be used. Even concentrated solutions of boric acid do not affect the color of methyl orange and hence this indicator can be used to determine the point at which all of the mineral acid but none of the boric acid in a mixture which contains both has been neutralized. Hence if a sample which contains any of the borates named is treated with an excess of hydrochloric acid and the mixture made to give a neutral reaction with methyl orange it will contain an amount of free boric acid which corresponds to the boric anhydride present. The free acid cannot be titrated directly even where phenolphthalein is used, but the addition of glycerine or mannitol increases its acidic properties to such an extent that this titration then becomes possible. If glycerine is used it must form about 30 per cent by volume of the entire mixture; if mannitol is used 2 per cent by weight is sufficient, and the end-point is more sharply defined.

The method is not affected by the presence of carbonates if the carbon dioxide which is liberated during the decomposition of the sample is expelled, but since boric acid is very slightly volatile long boiling must be avoided. The accuracy of the method depends largely upon the maintenance of the proper concentration of the reagents used.

Outline of the Method. Weigh out 1.5 gm. of the finely ground sample into a 200 cc. beaker, add 5 cc. of dilute hydrochloric acid, warm gently and stir with a glass rod until the sample seems to be completely decomposed, then add 10 cc. of water and heat to 80°. If a large amount of flocculent residue remains, filter on a very small filter but keep the volume of filtrate and washings to about 50 cc. Add a drop of methyl orange and then standard sodium hydroxide until the mixture has a clear lemon yellow color. Next add 3 drops of phenolphthalein and about 1 gm. of mannitol and finally titrate with the standard alkali to a permanent pink color. Add another half gram of mannitol and if the color fades continue adding alkali until it is restored. As equilibrium is attained but slowly more time should be allowed for this titration than for those previously described. Calculate the percentage of B_2O_3, assuming that each molecule has a neutralizing power of two.

V. The Analysis of Commercial Alkalies

Preliminary Statements. The alkalies of commerce consist mainly of the hydroxides, carbonates and bicarbonates of sodium and potassium. Their total alkalinity can be accurately determined by a direct titration with a standard acid, using methyl orange as indicator; or, by using the process of back titration and heating the solution to drive off carbon dioxide, other indicators may be used. It is sometimes necessary to distinguish between the alkalinity due to hydroxides and carbonates or between that due to carbonates and bicarbonates.

Methods for the Determination of Hydroxides and Carbonates. If a solution which contains both hydroxides and carbonates is titrated with a standard acid, using phenolphthalein, the color change takes place when the hydroxide has been completely neutralized and the carbonate changed into bicarbonate; hence the difference between the result obtained for total alkalinity and that obtained by this method represents the acid needed to neutralize the bicarbonate formed from the normal carbonate origi-

nally present and it is possible to calculate both the hydroxide and carbonate originally present. As the end-point in the latter titration is very unsatisfactory, this method is used only for approximate determinations.

A more satisfactory method of making this determination depends upon the addition of sufficient barium chloride to precipitate all of the carbonate and titration of the hydroxide in the resulting mixture.

Outline of Method for the Determination of the Hydroxide and Carbonate of Soda in Commercial Caustic Soda. Weigh accurately a glass weighing bottle of about 10 cc. capacity and transfer to it as rapidly as possible about 10 gm. of the roughly powdered and mixed sample, and again weigh accurately. Empty into a small beaker, add about 50 cc. of carbon-dioxide-free water and stir until the sample is dissolved. Pour into a 250 cc. graduated flask and rinse out both bottle and beaker with more water, cool to the normal temperature, dilute to exactly 250 cc. and mix thoroughly. The very small amount of insoluble residue sometimes found may be allowed to settle and is disregarded.

Measure out 25 cc. of the solution, add 50 cc. of water, a drop of methyl orange and titrate with the standard acid. Remove a second 25 cc. portion, add 50 cc. of water, 5 cc. of reagent barium chloride, a drop of phenolphthalein and titrate with the standard acid, adding the latter very slowly as the titration approaches completion. Calculate the percentages of sodium hydroxide and sodium carbonate present.

VI. Determination of Crude Protein in Flour

Theory of the Method. The proteins represent a group of extremely complex nitrogen-containing compounds, which form one of the three classes of nutrient materials present in foods. Altho the percentage of nitrogen present varies somewhat, experience has shown that protein can be determined with fair accuracy 'tiplying the percentage of nitrogen present by a factor which

varies somewhat with the nature of the proteid concerned. For the protein in flour the factor commonly used is 5.7, for that of meat 6.38 is used. The results obtained by this method are always designated as "crude protein."

When flour is heated with concentrated sulfuric acid the acid is gradually reduced to sulfur dioxide and water, while the carbon and hydrogen of the flour are oxidized to carbon dioxide and water and the nitrogen is changed to ammonium sulfate. When the resulting solution is distilled with an excess of a strong base ammonia is formed and distills over and can then be determined by titrating with a standard acid. Under certain conditions these operations can be carried out quantitatively, and form the basis of the Kjeldahl method which, with its various modifications, is used for the determination of all classes of nitrogen-containing compounds.

The Apparatus Needed. The Kjeldahl method involves two groups of operations. The "digestion" must be made in a round-bottomed flask, which is not easily broken by the large changes in temperature to which the different parts of it are subjected; flasks made of Jena or "pyrex" glass are commonly used. Since large amounts of sulfur dioxide and sulfur trioxide are formed this operation should be carried out in a hood which has a good draft, or each flask must be connected directly with a suction apparatus. The "distillation" must be made in a still, which is provided with a special form of still-head designed to prevent any of the boiling liquid from being carried over into the receiver while the distillation is in progress. Since the time needed for both of these operations may be long most laboratories are provided with special multiple-unit pieces of apparatus, in which the digestion and distillation of from three to twenty samples can be made simultaneously. In such an apparatus the condenser consists of a narrow trough of sheet copper thru which water slowly circulates; the condenser tubes are made of block tin, as this metal is not affected by dilute ammonium hydroxide.

Outline of Method of Procedure. Weigh out about 2 gm. of the sample into a 500 cc. Kjeldahl flask, which should be made of hard glass. Add 20 cc. of concentrated sulfuric acid, using it to rinse down any particles of the sample which adhere to the sides of the flask, and then add about 0.7 gm. of mercuric oxide for the purpose of increasing the speed of the reaction. Place the flask in an inclined position on a cold sand bath and heat gently for ten minutes or until violent frothing ceases, then raise the temperature to the boiling point and boil vigorously until a colorless solution is obtained. Remove from the rack, allow to cool slightly, and add a few grains of solid potassium permanganate, using sufficient to produce a slight but permanent pink or green color. Allow to cool, dilute to 200 cc. and again cool under the tap to the temperature of the room.

Add to the receiver of a distilling apparatus 10 cc. of semi-normal hydrochloric acid, 50 cc. of water and one drop of methyl orange. Place the delivery tube attached to the distillation apparatus inside the receiver and adjust the level of the latter until the end of the delivery tube touches the surface of the liquid in the receiver.

Add to the solution in the Kjeldahl flask 50 cc. of a 50 per cent solution of sodium hydroxide, then 10 cc. of a 5 per cent solution of potassium sulfide (to precipitate the mercury) and 2 gm. of granulated zinc (to prevent boiling over) and at once connect with the still-head by means of a good rubber stopper.

Heat to boiling and continue distilling until the volume of the solution in the receiver amounts to 200 cc. Remove the receiver, rinse out the delivery tube and titrate with a one-tenth normal solution of ammonium hydroxide. Calculate and report the percentage of crude protein present.

VII. Questions and Problems. Series 22

1. Calculate by the general formula the percentage of citric acid, a tribasic acid of the formula $C_6H_8O_7$, if the weight of mixture used was 0.643 gm., the volume of KOH solution used for the titration was 31 cc., and 1 cc. of KOH solution = 0.015 gm. of pure oxalic acid ($C_2H_2O_4 \cdot 2\,H_2O$).

2. Calculate the percentage of P_2O_5 in a solution of H_3PO_4 if the weight of solution used was 6.43 gm., volume of KOH solution used for the titration (with methyl orange) was 26 cc., and 1 cc. of KOH solution contained 0.016 gm.

3. Show how B_2O_3 could be determined in pure borax more easily than in calcium borate.

4. Explain why the $BaCO_3$ precipitated in the analysis of caustic soda has no effect on the titration. Is there any objection to using methyl orange for the titration? Is there any objection to filtering off and washing the $BaCO_3$ precipitate?

5. Calculate by the simplest method the volume of semi-normal acid required to neutralize the ammonium hydroxide produced by distilling 1 gm. of $FeSO_4(NH_4)_2SO_4 \cdot 6\,H_2O$ with an excess of KOH.

6. How would you prepare a solution of HCl so that each cubic centimeter should equal exactly 0.01 gm. of $NaNO_3$, when the latter was determined by reducing to an ammonium salt, distilling with an excess of KOH and titrating the distillate with the HCl solution?

SECTION IX

VOLUMETRIC PROCESSES INVOLVING OXIDATION

CHAPTER XLIV

GENERAL FEATURES OF PROCESSES INVOLVING OXIDATION

Definition of Oxidation and Reduction. The term oxidation is here used in its broadest sense and includes all changes in which any negative element or radical is added to, or any positive element or radical is removed from, the substance under consideration. Reduction represents the converse of this and the two actions are necessarily reciprocal, that is, where one element is oxidized some other must be reduced, and the total amount of oxidation effected must be equivalent to the total amount of reduction effected. If the distinction between positive and negative valence is recognized such reactions are always associated with changes in valence. According to this conception the valence of any uncombined element is always zero, that of any combined element corresponds to the number of positive or negative bonds of affinity represented by one atom of the element in the compound concerned. For example, the valence of arsenic is sometimes said to be three in both arsine and arsenic trioxide, but since hydrogen is a positive element the valence of arsenic in arsine s properly represented by -3, and since oxygen is a negative element the valence of arsenic in arsenic trioxide is properly represented by $+3$. Hence when arsine is oxidized to arsenic trioxide the valence of the arsenic changes from -3 to $+3$.

Definition of Oxidizing Capacity. In many of the substances used as oxidizing agents the valence of only one of the atoms in

the molecule changes; in such cases the amount of oxidation which can be effected by one molecule of the oxidizing agent is determined by the change in the valence of that element. In other cases two or more atoms change their valencies, and the amount of oxidation which can be effected by one molecule of the oxidizing agent is determined by the algebraic sum of the valence changes which all of the atoms in one molecule of the oxidizing agent undergo. The "oxidizing capacity" of any agent is defined as the total number of positive valencies furnished to, or of negative valencies taken from, the substance oxidized by one molecule of the agent. These statements can be illustrated by means of the following reactions:

(1) $CuSO_4 + Zn \rightarrow Cu + ZnSO_4$,

(2) $Fe(NO_3)_3 + Ag \rightarrow Fe(NO_3)_2 + AgNO_3$,

(3) $SnCl_2 + 2\,HgCl_2 \rightarrow SnCl_4 + 2\,HgCl$,

(4) $H_2S + I_2 \rightarrow S + 2\,HI$,

(5) $3\,H_2S + 8\,HNO_3 \rightarrow 3\,H_2SO_4 + 8\,NO + 4\,H_2O$.

In (1) the valence of zinc changes from 0 to + 2, that of copper from + 2 to 0. The oxidizing capacity of copper sulfate is here (+ 2) − (0), or + 2. The oxidizing capacity of zinc is (0) − (+ 2), or − 2, which is equivalent to saying that its reducing power is 2.

In (2) the valence of silver changes from 0 to + 1, that of iron from + 3 to + 2. The oxidizing capacity of ferric nitrate is here (+ 3) − (+ 2), or + 1, that of silver is (0) − (+ 1), or − 1.

In (3) the valence of tin changes from + 2 to + 4, that of mercury from + 2 to + 1. The oxidizing capacity of stannous chloride is (+ 2) − (+ 4), or − 2, that of mercurous chloride is (+ 2) − (+ 1), or 1.

In (4) the valence of sulfur changes from − 2 to 0, that of iodine from − 0 to − 1. The oxidizing capacity of hydrogen sulfide is (− 2) − (0), or − 2, that of iodine is (0) − (− 1), or 1.

In (5) the valence of sulfur changes from − 2 to + 6, that of

nitrogen from + 5 to + 2. The oxidizing capacity of hydrogen sulfide in this reaction is (− 2) − (+ 6), or − 8, that of nitric acid is (+ 5) − (+ 2), or + 3.

Oxidation and Ionization Changes. The five reactions can also be expressed in terms of the ionization changes concerned as follows:

(1) $\overset{++}{Cu} + \overset{--}{SO_4} + Zn \rightarrow Cu + \overset{++}{Zn} + \overset{--}{SO_4},$

(2) $\overset{+++}{Fe} + 3\,\overset{-}{NO_3} + Ag \rightarrow \overset{++}{Fe} + 3\,\overset{-}{NO_3} + \overset{+}{Ag},$

(3) $\overset{++}{Sn} + 6\,\overset{-}{Cl} + 2\,\overset{++}{Hg} \rightarrow \overset{++++}{Sn} + 6\,\overset{-}{Cl} + 2\,\overset{+}{Hg},$

(4) $2\,\overset{+}{H} + \overset{+-}{S} + I_2 \rightarrow S + 2\,\overset{+}{H} + 2\,\overset{-}{I},$

(5) $14\,\overset{-}{\overset{+}{H}} + 3\,\overset{--}{S} + 8\,\overset{-}{NO_3} \rightarrow 6\,\overset{+}{H} + 8\,NO + 4\,H_2O + 3\,\overset{--}{SO_4}.$

The first four of these reactions involve changes in the number of charges with which the different ions are associated only, and so far as these reagents are concerned oxidation can be defined as any process in which the number of positive charges associated with an element is increased, or the number of negative charges so associated is decreased; reduction would be defined by the converse statement. Furthermore, the number of positive charges gained or the number of negative charges lost is a measure of the oxidizing capacity of the reagent concerned.

In the fifth reaction there is also a change in the composition of one of the ions, that is, the NO_3 ion not only loses its negative charge but also two oxygen atoms, which become available as oxidizing agents. Hence this method of defining oxidation and reduction, which in many respects is an extremely convenient one to use, is not universally applicable, even when the process takes place in an aqueous solution.

Normal Values of Oxidizing Agents. The oxidizing capacity of oxidizing and reducing reagents measures one of the forms of chemical activity which these agents exhibit. Since the unit of

oxidizing capacity which has been adopted is the change in valence, and the unit of valence is that ordinarily exhibited by the hydrogen atom, the oxidizing capacity of a reagent is identical with E of the general formula, for volumetric determinations and the normal value of any oxidizing or reducing agent is found by dividing its molecular or atomic weight by its oxidizing capacity.

Meaning of Oxidation Potential. Altho four of the five reactions cited have very large constants, reactions (2) and many others of this class are appreciably reversible. In discussing the reversibility of such reactions it will be found desirable to conceive of every oxidizing and reducing agent as possessing a definite "oxidation potential." which is but one form of chemical potential, and to ascribe the ability of one reagent to oxidize another to the fact that its oxidizing potential is large as compared with that of the reagent oxidized. Thus the negligible reversibility of reaction (1) would be ascribed to the very large oxidation potential of copper sulfate as compared with that of metallic zinc. The reversibility of (2) would be ascribed to the fact that the oxidizing potential of ferric nitrate exceeds that of silver by a small amount only. The comparative values of the oxidizing potentials of the two reagents which react in any reaction involving oxidation is shown by the equilibrium constants of these reactions. The equilibrium constants of but few reactions of this type have been determined directly; they can be calculated more easily in many cases by use of the methods of electrochemistry.

Oxidation and the Theory of the Galvanic Cell. The electromotive force produced when reactions involving oxidation are made to take place in such a manner that electrical energy instead of heat is produced is found to be directly proportional to the equilibrium constant of the reaction. If, for example, reaction (1) is made to take place in the apparatus represented in Fig. 59, in which A represents a vessel containing a bar of metallic zinc in contact with a solution of zinc sulfate, and B a vessel containing a

bar of metallic copper in contact with a solution of copper sulfate the voltage shown by the voltmeter V measures the difference between the oxidizing potentials of copper sulfate and zinc. The voltage shown by such cells is found to increase with an increase in the concentration of the copper ion in the copper solution and to decrease with the concentration of the zinc ion in the zinc solution, and a formula, which was first suggested by Nernst, makes it possible to calculate at what concentrations all action would cease, that is, the concentrations of zinc and copper ions in a solution in which metallic zinc and copper sulfate would be in equilibrium. The ratio of these concentrations, that is, $(\overset{++}{Zn}) \div (\overset{++}{Cu})$ has been found to have the value 10^{38}. In a similar manner the equilibrium constant of reaction (2) has been found to have the value 0.1.

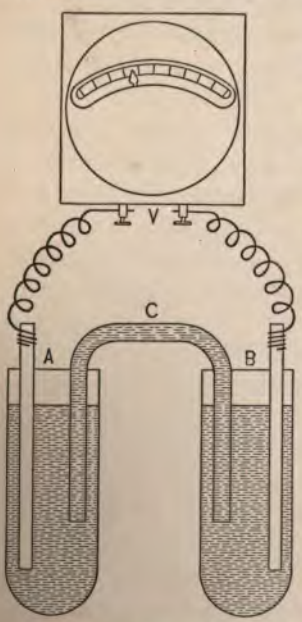

Fig. 59. — Diagram of a Galvanic Cell

Determination of Electrode Potentials. The electromotive force of a galvanic cell is determined by the difference between the electrode potentials at the two electrodes of which the cell is composed. The difference of potential at each electrode is determined by the oxidizing potential of the agent which undergoes a change at the electrode. Thus the electrode potential of copper sulfate in contact with copper depends upon the oxidizing potential of the copper ion, that is, upon the ease with which it gives up its positive charges to some substance. Hence the oxidizing potentials of the different oxidizing agents are proportional to the electrode potentials shown by these agents when they undergo a reaction in a galvanic cell.

If a numerical value is arbitrarily assigned to some particular electrode and the electromotive force of the cells formed by combining this electrode with a number of other electrodes is determined a series of numbers representing the comparative values of the electrode potentials of these electrodes can be calculated. In attempting to prepare electrodes, whose potential differences shall represent the oxidizing potentials of reagents which are not conductors of the metallic class and which do not yield conductors of the metallic class, it is necessary to make use of a metal like platinum which is a good conductor and whose action on the solution is so small that it can be neglected. Thus in measuring the oxidizing potential of hydrogen it is necessary to use an electrode which measures the potential difference between gaseous hydrogen and a solution of the hydrogen ion. This can be effected by use of the device represented in Fig. 60.* It consists of a sheet of platinum foil bent like the letter *S*, which is surrounded by a bell-shaped glass tube of such a form that the lower half of the foil is in contact with the solution and the upper half with pure gaseous hydrogen, which is made to circulate through the apparatus continuously. The potential difference shown by such an electrode also depends upon the oxidizing potentials of such reagents as may be added to the solution in contact with it, and hence it can be used to measure the oxidizing potentials of reagents like ferric salts or chromic acid.

Fig. 60. — Hydrogen Electrode

A Table of Electrode Potentials. In the table which appears below, the oxidizing agents whose formulæ appear in the first column have been arranged with respect to the numerical value of the electrode potential to which they give rise when they react in a galvanic cell in the manner indicated in the second column.

* Hildebrand, Jour. of Am. Chem. Soc., **35**, 847.

TABLE OF ELECTRODE POTENTIALS

Oxidising agent	Reaction concerned	Conc. of solution	Electrode potentials
$KMnO_4$ + acid	$MnO_4^- \rightarrow Mn^{++}$	.....	$<+1.640$
Cl_2	$Cl_2 \rightarrow 2\,Cl^-$	$(Cl^-)=1$	$+1.640$
K_2CrO_4 + acid	$Cr_2O_7^{--} \rightarrow Cr^{+++}$	.....	$<+1.270$
Br_2	$Br_2 \rightarrow 2\,Br^+$	$(Br^+)=1$	$+1.270$
Ag^+	$Ag^+ \rightarrow Ag^+$	$(Ag^+)=1$	$+1.076$
Fe^{+++}	$Fe^{+++} \rightarrow Fe^{++}$	$(Fe^{+++})=(Fe^{++})$	$+1.016$
I_2	$I_2 \rightarrow 2\,I^-$	$(I^-)=1$	$+0.80$
Cu^{++}	$Cu^{++} \rightarrow Cu^{++}$	$(Cu^{++})=1$	$+0.606$
$(H)^+$	$(H)^+ \rightarrow H^+$	$(H^+)=1$	$+0.277$
$(Pb)^{++}$	$(Pb)^{++} \rightarrow Pb^{++}$	$(Pb^{++})=1$	$+0.129$
$(Cd)^{++}$	$(Cd)^{++} \rightarrow Cd^{++}$	$(Cd^{++})=1$	-0.143
$(Zn)^{++}$	$(Zn)^{++} \rightarrow Zn^{++}$	$(Zn^{++})=1$	-0.493
$(Mg)^{++}$	$(Mg)^{++} \rightarrow Mg^{++}$	$(Mg^{++})=1$	-1.273
$(Na)^+$	$(Na)^+ \rightarrow Na^+$	$(Na^+)=1$	-2.483
$(Li)^+$	$(Li)^+ \rightarrow Li^+$	$(Li^+)=1$	-2.744

The figures given in the last column represent the electrode potentials when the concentration of the solution is that represented in the third column. In general, any reagent which appears in the upper part of the table should oxidize any reagent which appears below it, that is, if the two reagents are brought together the one which appears first in the table reacts in the manner indicated in the second column; that which appears later reacts in the reverse direction of that indicated in the second column. The value of the equilibrium constants between any two such reagents is large in proportion as the difference between the corresponding electrode potentials is large. Thus the very large equilibrium constant of reaction (1) accords with the difference between the electrode

potentials of the $\overset{+}{Cu} \rightarrow Cu$ and the $\overset{+}{Zn} \rightarrow Zn$ electrodes, that is, $(+0.606) - (-0.493)$, or 1.099 volts. The smaller equilibrium constant of reaction (2) accords with the smaller difference between the $\overset{+}{Ag} \rightarrow Ag$ and the $\overset{+++}{Fe} \rightarrow \overset{++}{Fe}$ electrodes, that is, $(+1.076) - (+1.016)$, or 0.06 volt.

The Recognition of End-Points. The oxidizing potentials of mixtures made by adding together equivalent amounts of two reagents which react completely is zero. If the reaction concerned was not absolutely complete such mixtures would show a slight positive or negative oxidation potential when equivalent amounts were present. It is possible to measure the electromotive force of a galvanic cell, one electrode of which consists of a hydrogen electrode placed in a mixture containing equivalent proportions of two oxidizing agents, with great accuracy. If such a measurement has been made, the true end-points of titrations between solutions containing these reagents can be ascertained by carrying the titration to the point at which the electromotive force of the cell corresponds with that previously found. The electromotive force of such a cell also changes very greatly with very slight changes in the ratio between the quantities of the two reagents present in the neighbo hood of the point at which this ratio is one; therefore the true end-point can also be determined by noting the rate of change in the value of the electromotive force of the cell during the titration.

These methods of determining the end-points of processes of this class are not widely used at present altho they possess decided advantages. In most cases the end-point is determined by means of an indicator. The number of indicators available is very limited and with but few exceptions they can only be used for one titration; hence their action will be considered in discussing the particular titration in which they are used.

CHAPTER XLV

DETERMINATIONS WITH POTASSIUM PERMANGANATE

I. Potassium Permanganate as an Oxidizing Agent

Oxidizing Potential and Oxidizing Capacity. This is a particularly useful oxidizing agent since solutions of it act completely and instantaneously with a large number of reagents. Its oxidizing potential has not been measured accurately, but exceeds that of all the reagents listed in the table on page 320.

Its reaction with a ferrous salt, which is typical of a large number of oxidations effected by it in an acid solution, is represented by the expression:

(1) $2\,KMnO_4 + 10\,FeSO_4 + 8\,H_2SO_4 \rightarrow 5\,Fe_2(SO_4)_3 + 2\,MnSO_4 + K_2SO_4 + 8\,H_2O.$

Assuming that the degree of oxidation of the potassium has a constant value of $+1$, and that of sulfur in sulfates is $+6$ the degree of oxidation of the manganese changes from $(2 \times 4) - 1$, or $+7$, to $(2 \times 4) - 6$, or $+2$, and hence the oxidizing capacity of one molecule of the permanganate is 5. Its behavior in all such reactions may also be represented by the expression:

(2) $2\,KMnO_4 \rightarrow K_2O + 2\,MnO + 5\,O.$

This equation represents an ideal conception only and will not take place in an aqueous solution unless some acid is present, which can take up the oxides of potassium and manganese, and some reducing agent is present to take up the available oxygen.

Its use in a neutral solution is illustrated by its reaction with a ese salt according to the expression:

$$_1O_4 + 3\,MnCl_2 + 2\,H_2O \rightarrow 5\,MnO_2 + 2\,KCl + 4\,HCl.$$

In this reaction the degree of oxidation of the manganese changes from $(2 \times 4) - 1$, or $+7$, to (2×2), or $+4$, and the oxidizing capacity of one molecule of the permanganate is 3. Its behavior in reactions of this type is therefore correctly represented by the expression:

(4) $$2\,KMnO_4 \rightarrow K_2O + 2\,MnO_2 + 3\,O.$$

This reaction like (2) is an ideal conception and does not take place with appreciable velocity unless some agent which is capable of utilizing the available oxygen is present. It should be noted that the normal value of potassium permanganate is either one-fifth or one-third of its molecular weight according to whether it is used in an acid or in a neutral solution.

Factors Which Affect Permanganate Reactions. When this reagent is used in an acid solution some judgment must be exercised with respect to the character and concentration of the acid present. Nitric acid is usually to be avoided, since it is itself a strong oxidizing agent, and many of the organic acids are objectionable since some of them reduce potassium permanganate. Hydrochloric is often objectionable owing to the possibility of a reaction taking place, which is represented by the expression:

(5) $$2\,KMnO_4 + 16\,HCl \rightarrow 2\,KCl + 2\,MnCl_2 + 5\,Cl_2 + 8\,H_2O.$$

In the presence of certain metallic ions, especially iron, gold, platinum and cadmium, this reaction takes place even in moderately dilute cold solutions, and hence erroneous results and unsatisfactory end-points are obtained in the titration of such solutions. In the absence of these ions the presence of moderate concentrations of hydrochloric acid is not objectionable. Various theories have been advanced to explain this phenomenon, but the assumption that the ions named act as positive catalyzers is as satisfactory as any. The effect of these ions is largely inhibited by the addition of large amounts of a manganous salt, that is, the manganous ion seems to act as a negative catalyzer for reaction (5). Altho it is possible to counteract the effect of moderate concen-

trations of hydrochloric acid, even when positive catalyzers are present, by the addition of manganous sulfate the conditions which make such an addition necessary should be avoided whenever possible.

In view of the above statements sulfuric acid is usually employed in all titrations with potassium permanganate which are effected in acid solutions. The concentration of hydrogen ion necessary to make such reactions complete and instantaneous varies. Reaction (1) is found to be sufficiently complete even when 1 cc. of concentrated acid per 100 of solution is present; that is, where $(\overset{+}{H}) = 0.35$. If the amount of acid added exceeds 40 cc. per 100 of solution, especially if the temperature is much above 20°, a further secondary reaction becomes possible which is expressed by the equation

(6) $2\,KMnO_4 + 3\,H_2SO_4 \rightarrow K_2SO_4 + 2\,MnSO_4 + 2.5\,O_2 + 3\,H_2O.$

Determination of the End-Point. A single drop of a one-tenth normal solution of potassium permanganate, that is, one containing 3.16 gm. per liter, imparts an easily recognizable pink color to 200 cc. of water. Since potassium and manganese sulfates impart no color to aqueous solutions no special indicator need be used, provided the compound which is oxidized yields products whose colorific value is sufficiently small. Thus the true end-point of reaction (1) can be easily and accurately recognized, since the yellow color imparted to the solution by the small concentration of ferric ion present at the end-point of the titration is negligible as compared with the pink color produced by one drop of [illegible]nate. In other reactions, such as the reaction by [illegible]anides are oxidized to ferricyanides, the red color [illegible] solution before the end-point is reached leads to a

[illegible] **Uses.** The more important determinations which [illegible] the use of a standard permanganate solution may be conveniently classified under four groups.

First, the direct oxidation of certain metallic elements from a lower to a higher degree of oxidation, including, in addition to iron and manganese, the elements copper, tin, arsenic, antimony, titanium, molybdenum, tungsten and uranium. Some of these processes are unsatisfactory or are less convenient than other methods.

Second, the direct oxidation of certain inorganic acids or their salts, including nitrous acid, which is oxidized to nitric; sulfurous acid, which is oxidized to sulfuric; sulfhydric acid, which is oxidized to sulfur and water; ferrocyanic acid, which is oxidized to ferricyanic acid; sulfocyanic acid, which is oxidized to hydrocyanic and sulfuric acids, and hydrogen peroxide which is oxidized to oxygen and water.

Third, the direct oxidation of certain organic substances such as oxalic and formic acids, and tannin.

Fourth, a large number of indirect determinations. They would include elements which form insoluble compounds with the acids enumerated in the second and third groups, and which can therefore be separated from solution, treated with a stronger acid and the liberated acid titrated. Of especial interest is a method for the determination of phosphorus which involves precipitating that element as ammonium phosphomolybdate, separating from the solution, redissolving and reducing the molybdenum in the solution, and titrating the latter.

II. Preparation and Standardization of a Permanganate Solution

Preparation. Nearly all of the determinations commonly made with potassium permanganate are carried out in an acid solution. A solution of one-tenth normal strength, assuming that the oxidizing power is five, is usually prepared; it should contain 3.16 gm. per liter. If it becomes desirable to use such a solution for determinations which are carried out in the absence of an acid it should be remembered that it is only 0.06 normal for all such determinations.

The potassium permanganate sold by dealers, even tho marked C.P., usually contains small amounts of manganese dioxide; further, when dissolved in water more manganese dioxide slowly separates owing to the reducing action of the small amount of organic matter usually present even in distilled water, and to the action of light. The insoluble dioxide seems to catalyze this action and leads to the production of further amounts of dioxide. Hence it is desirable to allow the prepared solution to stand for twenty-four hours, that is, until the easily oxidizible organic matter is entirely consumed, then to remove the dioxide and other insoluble impurities by filtering thru asbestos, and to preserve the solution in a perfectly clean bottle which is protected from strong sunlight. Under these conditions a solution can be preserved for many months without appreciable reduction in strength.

Methods of Standardization. A large number of substances have been and are still used for the standardization of permanganate solutions. Pure metallic iron, which has been deposited on a weighed platinum dish by means of an electric current, has many advantages, but since this deposit contains small amounts of carbon, which has a large reducing power, the results are slightly inaccurate. Pure ferrous ammonium sulfate, $FeSO_4(NH_4)_2SO_4 \cdot 6\,H_2O$, is still more convenient but the purity of the salt sold under this name cannot be assured, and it is necessary to test each sample for its reducing power by some independent process. Oxalic acid is sometimes used, but unless prepared under certain definite conditions its purity cannot be depended upon.

The most satisfactory standard is sodium oxalate, which can be prepared to correspond with the formula $Na_2C_2O_4$ under conditions first determined by Sorensen.* The proper conditions for its preparation, and methods of ascertaining its purity were more carefully elaborated by Blum,† and samples of guaranteed purity can now be purchased from the Bureau of Standards at Washington.

* Zeit. für analyt. Chemie, **42,** 512 (1903).

† Jour. of Am. Chem. Soc. **34,** 123 (1912).

Conditions for Titration of Sodium Oxalate. Oxalic acid can be completely oxidized by potassium permanganate according to the reaction:

$$(7) \quad 5\,C_2H_2O_4 + 2\,KMnO_4 + 3\,H_2SO_4 \rightarrow 10\,CO_2 + K_2SO_4 + 2\,MnSO_4 + 8\,H_2O.$$

At ordinary temperatures the velocity of this reaction is very small, but at 60° it proceeds almost instantaneously, and after the reaction has once been initiated it proceeds fairly rapidly, even if the temperature falls below 60°. The concentration of hydrogen ion necessary to make the reaction complete and instantaneous is somewhat greater than that necessary for the oxidation of iron. Either sulfuric or hydrochloric acid can be used to supply the necessary concentration of hydrogen ion.

Outline of Method of Procedure. Weigh out 6.32 of pure crystallized permanganate into a 400 cc. beaker, add 250 cc. of water, warm slightly and stir for a few minutes, then pour the clear supernatant liquid into a 2000 cc. flask; again add water, warm, stir and pour into the flask, and continue this cycle of operations until all of the salt has been brought into solution. Altho the salt is highly soluble the rate of solution is low and some time can be saved by proceeding as directed. Finally, dilute to 2000 cc. and allow to stand for at least 24 hours. Prepare an asbestos filter and connect with a clean two-liter bottle as shown in Fig. 58, then filter the permanganate solution thru it. Keep the bottle in a dark closet or cover with opaque paper.

Dry some pure sodium oxalate (Sorensen) for a half hour at a temperature of 250°. Weigh out from 0.25 to 0.3 gm. into a 400 cc. beaker, add 200 cc. of water, then slowly add 5 cc. of concentrated sulfuric acid. Heat the solution to 80° and titrate slowly, adding the permanganate solution until a faint but permanent pink color appears.

Divide the weight of sodium oxalate weighed out by the volume of permanganate solution used and then divide the quotient by

the weight of sodium oxalate present in a normal solution of that reagent to determine the relation of the permanganate solution to normality. Since one molecule of sodium oxalate yields one of oxalic acid, and since the reducing power of the latter is two, 1 cc. of normal sodium oxalate should contain one two-thousandth of its molecular weight expressed in grams.

III. Determination of Iron in Cast Iron

Interfering Elements. Cast iron usually contains several per cent of silicon and carbon and smaller amounts of manganese, sulfur and phosphorus. If dissolved in sulfuric acid the silicon forms silicic acid, the manganese forms manganous sulfate, the phosphorus forms phosphorous acid and that part of the carbon which exists in the form of graphite separates as such, but that part which exists as iron carbide (Fe_3C) yields more or less volatile hydrocarbons. Even if the resulting solution is heated to boiling it will be found to reduce more iron than would correspond to the iron present. The simplest method of overcoming this difficulty is to destroy these reducing substances by a preliminary treatment with potassium permanganate, reduce the iron necessarily oxidized by this treatment and again titrate with the permanganate solution. If a slight excess of permanganate is used and the solution heated during the preliminary oxidation, a more complete oxidation of these reducing substances than is effected in the final titration can be assured, and experience shows that the products formed, which are in part carbon dioxide and water, are not reduced by the method used for the reduction of the iron.

Methods of Reducing Iron. The reducing agents employed for this purpose must be slightly soluble solids or gases, otherwise the excess necessarily used cannot be removed. Of the possible solid reagents, metallic zinc, aluminum, magnesium and lead are most frequently used. The reactions concerned can be represented by the expression:

$$Fe_2(SO_4)_3 + Zn \rightarrow 2\,FeSO_4 + ZnSO_4$$

Reduction with these reagents is always effected in a solution strongly acidified with sulfuric acid, but the hydrogen which is also produced has no effect on the degree of oxidation of the iron, and reduction takes place only at the surface of the metal used. Of the metals named, aluminum acts somewhat more rapidly than zinc or magnesium, and is not acted upon to the same extent by the free sulfuric acid present; on the other hand, it is very difficult to obtain the metal sufficiently free from iron.

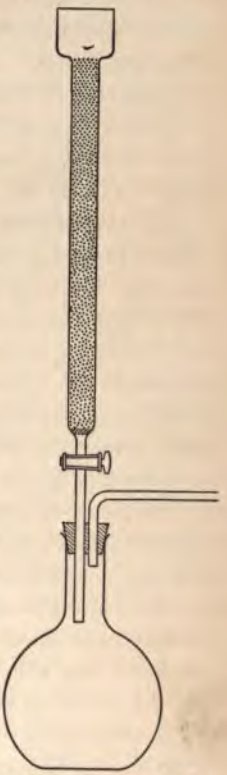

Fig. 61. — Jones Reductor

Of the gaseous reducing agents, hydrogen sulfide, which is oxidized by ferric iron to sulfur and water, and sulfur dioxide, which is oxidized to sulfuric acid, are most frequently used. Both reagents reduce the iron rapidly and completely, and boiling for a few minutes expels the excess used completely. The finely divided sulfur which is formed when the former reagent is used is without appreciable action on the permanganate solution unless the solution is hot. When sulfur dioxide is used the best results are obtained when the solution contains a very slight excess of free acid only.

Use of the Jones Reductor. Since reduction takes place only at the surface of the metal used, the process is a slow one, especially if the solution has a large volume. If, however, the metal is reduced to a fine state of division and the iron solution passed slowly thru a tube filled with it, both the total amount of metal consumed and the time required for complete reduction are very greatly reduced. This principal is made use of in the Jones reductor represented in Fig. 61. Its use often decreases the time

needed for complete reduction from two hours to fifteen minutes. In using it care should be taken to prevent air from coming into contact with the zinc while the solution is being reduced, as it has been shown that a small amount of hydrogen peroxide, which is subsequently oxidized by the permanganate, may be formed under these conditions.

Outline of Method of Procedure. Prepare the sample either by drilling out about 10 gm. of fine powder, or by turning off an equal amount of thin shavings from the metal to be analyzed. Weigh out 0.25 gm. of the powdered sample into a 200 cc. beaker, add 25 cc. of dilute sulfuric acid, warm gently and allow to stand until no more hydrogen is evolved, and only gelatinous silicic acid and graphite, which float in or on the solution, remain. Add sufficient permanganate solution to impart a deep red color to the mixture, even after it has been warmed to 50°. Dissolve the precipitate of manganese dioxide, which usually separates, by heating and if necessary adding a very small amount of sodium sulfite and expelling the sulfur dioxide formed. Filter the mixture, using a 9 cm. filter and washing the latter free from iron, but endeavor to keep the total volume less than 100 cc.

Prepare a Jones reductor as follows: Dissolve 5 gm. of metallic mercury in 50 cc. of dilute nitric acid and dilute the solution to 250 cc. Add 250 gm. of granulated zinc, which is fine enough to pass a 20- but not fine enough to pass a 30-mesh sieve. Stir the mixture for a few minutes, then pour off the solution and wash the residual metal until free from nitric acid and nitrates. Place a disk of perforated platinum foil in the bottom of the reductor tube, cover this with a thin layer of glass wool and finally fill with the amalgamated zinc as far as the cuplike enlargement at the top. Connect the tube with the flask and the latter with a suction pump. Rinse out the tube by passing thru it 250 cc. of dilute sulfuric acid (5 of conc. acid to 100 of water) being careful never to let the liquid get below the top of the zinc column.

Next pass the iron solution thru the reductor, regulating the

pump so as to require about fifteen minutes for the passage of the entire solution, and as soon as the latter reaches the top of the zinc column rinse out by the use of 200 cc. of dilute sulfuric acid.

Remove the flask from the reductor tube and titrate the solution without delay. Calculate the percentage of iron present in the solution, noting that since its degree of oxidation is increased from two to three its reducing power is one.

IV. Determination of Potassium Nitrite in the Commercial Salt

Theory of the Method. The action of potassium permanganate on nitrous acid is represented by the expression:

(9) $$5\,HNO_2 + 2\,KMnO_4 + 3\,H_2SO_4 \rightarrow 5\,HNO_3 + K_2SO_4 + 2\,MnSO_4 + 3\,H_2O.$$

When nitrous acid is titrated with potassium permanganate in a dilute solution the reaction is complete and instantaneous as long as either reagent is present in moderately large excess, but as the end-point is approached the rate of action becomes extremely slow, and it is not possible to determine the correct end-point with even approximate accuracy. If, however, an excess of permanganate is added to the nitrous acid solution the latter is rapidly and completely oxidized, and the excess of permanganate used can be determined by titrating with a standard solution of a ferrous salt, or by adding an excess of a ferrous salt and titrating back with the permanganate; there is little danger that reaction (9) will reverse, that is, that nitric acid will be reduced to nitrous acid by either the ferrous or manganous salt present, provided the solution is cold and dilute.

Potassium nitrite is decidedly hygroscopic and an average sample cannot be obtained unless it is thoroughly mixed and unless several grams are weighed out. It does not ordinarily contain any other substances which interfere with the titration.

Outline of Method of Procedure. Prepare a solution of ferrous sulfate by dissolving 28 gm. of the crystallized salt ($FeSO_4 \cdot 7\ H_2O$) in water, adding 10 cc. of concentrated sulfuric acid and diluting to one liter. Determine the volumetric relation between this and the permanganate solution by titrating 25 cc.

Weigh out 2 gm. of the well-mixed sample in a weighing bottle, dissolve and dilute to 250 cc. in a graduated flask and mix thoroughly. Remove 25 cc. of this solution to a 250 cc. beaker or Erlenmeyer flask, add exactly 50 cc. of the permanganate solution and allow to stand for a few minutes. Next add 5 cc. of dilute sulfuric acid and shake or stir for a few minutes, then add 25 cc. of the ferrous sulfate solution and finally titrate with the permanganate solution. Calculate the volume of permanganate solution which would be equivalent to the 25 cc. of ferrous sulfate solution used and subtract from the total volume of permanganate employed. Calculate the weight of KNO_2 corresponding to this volume of permanganate, assuming that the reducing power of the KNO_2 is two. Report the per cent present in the sample.

V. Determination of Calcium in Limestone

Theory of the Method. The insolubility of calcium oxalate and the ease with which oxalic acid can be titrated with potassium permanganate forms the basis of an exceedingly useful indirect method for the determination of this element. The accuracy of the method depends, first, upon the completeness with which the oxalate can be separated from the solution and from any other oxalates which may be occluded or co-precipitated with it; second, upon the completeness of the reaction:

$$CaC_2O_4 + H_2SO_4 \rightarrow CaSO_4 + H_2C_2O_4, \tag{10}$$

and third upon the equilibrium constant of reaction (7). The first of these factors is discussed in Chapter XXIV and it is there shown that even in the presence of magnesium the error involved in the separation can be made very small. The constant for

reaction (10) is large since the dissociation constant of oxalic acid is much smaller than that of sulfuric acid. The constant for reaction (7) as shown in an earlier paragraph of this chapter is also very large.

Outline of Method of Procedure. Weigh out 0.5 gm. of the sample into a 250 cc. beaker, cover with a watch glass and introduce 10 cc. of dilute hydrochloric and 5 of dilute nitric acid, and warm on a sand or steam bath until the decomposition seems to be complete, and fumes of NO and Cl are no longer given off. Rinse off and remove the watch-glass cover and bring the volumes of the solution to 100 cc.

Heat the solution nearly to boiling, add a slight excess of ammonium hydroxide, digest for a few minutes, then filter on a 9 cm. filter and wash until free from soluble salts. If the volume of iron and aluminum hydroxide thus obtained is large, redissolve and reprecipitate and combine the two filtrates.

Dilute the filtrate to 300 cc., add a drop of methyl orange indicator and dilute hydrochloric acid until the solution gives a neutral reaction. Heat to boiling, add 18 cc. of oxalic acid solution and stir for a few minutes; if a precipitate does not separate add a single drop of ammonium hydroxide and stir rapidly. After about ten minutes add diluted (1 : 4) ammonium hydroxide slowly and with constant stirring until the solution is distinctly alkaline; finally allow the mixture to stand for at least an hour.

Filter off the precipitate on a 9 cm. filter and wash both precipitate and filter very thoroughly, that is, until the washings show no action on a drop of permanganate solution even after acidifying and heating to 80°.

Remove the filter from the funnel, open it out and flatten against the side of a 400 cm. beaker. Rinse the precipitate adhering to the filter into the bottom of the beaker and bring the total volume up to 200 cc. Add 5 cc. of concentrated sulfuric acid, heat to 80° and titrate with the permanganate as in the standardization.

Calculate and report the percentage of CaO present, noting that

since one atom of calcium precipitates one molecule of calcium oxalate and the latter yields one molecule of oxalic acid, which has a reducing power of two, the correct per cent is given by the formula:

$$\frac{\text{Mol. wt. CaO}}{2 \times 1000} \times N \times \frac{\text{vol. } KMnO_4}{\text{wt. of sample}} \times 100 = \text{per cent CaO},$$

in which N represents the normality of the solution used.

VI. Questions and Problems. Series 23

1. Outline the method of reasoning by which you decide upon the reducing capacity of the two metallic elements and the two acids oxidized by potassium permanganate according to the equations given below:

$$2\,KMnO_4 + 5\,Ti_2(SO_4)_3 + 8\,H_2SO_4 \rightarrow 10\,Ti(SO_4)_2 + K_2SO_4 + 2\,MnSO_4 + 8\,H_2O,$$

$$2\,KMnO_4 + 5\,U(SO_4)_2 + 2\,H_2O \rightarrow 5\,(UO_2)SO_4 + K_2SO_4 + 2\,MnSO_4 + 2\,H_2SO_4,$$

$$14\,KMnO_4 + Mo_{24}O_{37} + 21\,H_2SO_4 \rightarrow 24\,MoO_3 + 14\,MnSO_4 + 7\,K_2SO_4 + 21\,H_2O,$$

$$12\,KMnO_4 + 10\,HCNS + 8\,H_2SO_4 \rightarrow 10\,HCN + 6\,K_2SO_4 + 12\,MnSO_4 + 8\,H_2O.$$

—. ·ut the reactions in which potassium permanganate oxidizes tin to the quadrivalent condition, and arsenic and antimony › the quinquivalent condition in acid solutions.

ts on calcium carbide C_2H_2 is produced, when it acts › CH_4 is produced, what are the probable formulæ of

phosphorus would be represented by one cc. of a one- of potassium permanganate assuming that the phos- ›d as $(NH_4)_3PO_4 \cdot 12\,MoO_3$, the precipitate dissolved and ‹d the latter titrated by the reaction given in the first

›f copper would be represented by one cc. of a one-tenth ›otassium permanganate, assuming that the copper was 'NS and the precipitate oxidized to $CuSO_4$, HCN and nganate solution?

6. What weight of potassium permanganate should be present in one cc. of the solution in order that each cc. should represent three milligrams of manganese if precipitated by reaction (3)?

7. How much antimony would be represented by one cc. of a solution containing 3 gm. of $KMnO_4$ per liter, assuming that the antimony is precipitated as sulfide, the sulfide added to a solution of ferric sulfate and the reduced iron titrated according to the reactions:

$$5\,Fe_2(SO_4)_3 + Sb_2S_3 + 6\,H_2O \rightarrow 2\,HSbO_3 + 3\,S + 10\,FeSO_4 + 5\,H_2SO_4,$$
$$2\,KMnO_4 + 10\,FeSO_4 + 8\,H_2SO_4 \rightarrow 5\,Fe_2(SO_4)_3 + K_2SO_4 + 2\,MnSO_4 + 8\,H_2O$$

8. In determining iron in a sample of cast iron which contained 95 per cent of iron and 3 per cent of carbon, one-tenth of the latter remains in solution as C_2H_2 and is oxidized to carbon dioxide and water by the permanganate, what is the error in the determination of iron?

9. Suggest indirect methods for the determination of the elements arsenic cobalt and zinc in which potassium permanganate is used as the oxidizing agent.

10. In the determination of iron in cast iron, (a) why dissolve in H_2SO_4 rather than HCl or HNO_3, how would the result be affected (b) if the precipitate of MnO_2 was not dissolved, (c) if an excess of Na_2SO_3 was used and the solution was not heated, (d) if the H_2SO_4 used to wash out the reductor contained small amounts of HNO_3, (e) if the sample contained small amounts of Cu, or Mn, or Cr or Al?

CHAPTER XLVI

DETERMINATIONS WITH POTASSIUM DICHROMATE

I. Potassium Dichromate as an Oxidizing Agent

Oxidizing Potential. This reagent is used as an oxidising agent in an acid solution, and altho in its general behavior it resembles potassium permanganate the data given in the table on page 320 shows that its oxidizing potential is somewhat less. The salts of certain metals which are completely oxidized from a lower to a higher degree of oxidation by the permanganate are only partially oxidized by the dichromate; further, the dichromate has but little action upon oxalic and other organic acids unless the solutions used are hot and concentrated. Its solutions are so stable that they can be preserved for months without loss of strength, even when exposed to strong sunlight.

Oxidizing Capacity. The oxidizing capacity of this reagent is best shown in the reaction which takes place when it is brought into contact with a ferrous salt, and which can be expressed as follows:

(1) $K_2Cr_2O_7 + 6\,FeCl_2 + 14\,HCl \rightarrow 6\,FeCl_3 + 2\,KCl + 2\,CrCl_3 + 7\,H_2O$

Since this reaction involves the reduction of the chromium from chromium trioxide, whose degree of oxidation is represented by + 6, to a salt of chromium, in which the degree of oxidation is represented by + 3, the oxidizing power of one molecule of the dichromate, which can be regarded as a combination of one molecule of potassium oxide with two of chromium trioxide, is two times the difference between six and three or six. The decomposition of the dichromate may also be represented by the equation:

(2) $K_2Cr_2O_7 \rightarrow K_2O + Cr_2O_3 + 3O.$

The latter, like the corresponding equation for the permanganate, is an ideal conception only, and does not take place in solution unless it contains a sufficient amount of acid to take up the oxides of potassium and chromium, and a reducing agent of sufficient strength to utilize the available oxygen.

Conditions Necessary for the Titration. Reaction (1) is both complete and instantaneous if a concentration of hydrogen ion corresponding to that represented by about 1 cc. of the concentrated hydrochloric acid per 100 of solution is present. There is but little danger of interaction with the acid itself and consequent liberation of chlorine, unless the solution is hot, or unless the concentration of acid exceeds forty times the minimum value named. Sulfuric acid, if added in amounts sufficient to yield concentrations of hydrogen ion equal to that resulting from the minimum concentration of hydrochloric acid named, can also be used to acidify the solution.

Determination of the End-Point. The intensity of the yellow color of solutions containing Cr_2O_7 ions is much less than the red color of those containing corresponding concentrations of MnO_4 ions, and furthermore the $\overset{+++}{Cr}$ ions formed when $\overline{Cr}_2O_7$ or $\overline{Cr}O_4$ are reduced, impart a very intense green color to the solution.

In the titration of iron salts the end-point can be determined by the use of a test which distinguishes between ferrous and ferric ions; in the titration of other reducing agents it becomes necessary to add an excess of the dichromate solution, and to determine the amount added in excess by titrating back with a standard solution of a ferrous salt.

Potassium ferricyanide reacts with a ferrous salt as follows:

(3) $$2\,K_3Fe(CN)_6 + 3\,FeCl_2 \rightarrow Fe_3[Fe(CN)_6]_2 + 6\,KCl.$$

The ferrous ferricyanide produced is insoluble even in acid solutions, and has a very intense blue color. It is possible to recognize by this test one part of ferrous ion in one hundred thousand of water. Ferric salts do not react with the reagent, but when the

concentration of the ferric ions is sufficiently large and that of the ferrous ions small, the yellow color of the ferric ion masks the blue coloration normally produced by the indicator and gives a green coloration.

If the indicator is added directly to the solution in which the titration is being made the ferrous ferricyanide precipitate produced remains unaffected, even after an excess of potassium dichromate has been added. It becomes necessary, therefore, to use this reagent as an "outside indicator," that is, to remove and test a drop of the solution from time to time during the titration. These tests will first yield a deep blue precipitate; slightly before the true end-point is reached they will show a green coloration; at the true end-point a clear yellow; and when an excess of dichromate is present a slight brown.

The accuracy of this method of determining the end-point is affected by a number of details. If the indicator solution used has stood for more than twenty-four hours in strong sunlight it will be found to contain some ferrocyanide and hence will give misleading results. If its concentration exceeds one-fifth of one per cent, the end-points are not clearly defined. Further, the size of the drop of indicator solution used, as compared with the size and concentration of the drop of solution which is tested affect the final color. Even those tests which show no reaction for ferrous iron at first, gradually develop a blue color, owing to the gradual reduction of some of the iron by the light, and hence a definite time interval should be observed in judging whether the true end-point has been reached.

Special Advantages of Potassium Dichromate. This reagent does not oxidize hydrochloric acid, even in the presence of iron salts, and hence it can often be used when potassium permanganate cannot be employed. Since most of the ores of iron cannot be brought into solution without the use of hydrochloric acid, and since the iron in such ores can be reduced more rapidly by the use of stannous chloride than by any other method, the process is

peculiarly adapted to the determination of iron in iron ores. Altho it oxidizes a number of other metals by reactions which are both complete and instantaneous it is rarely used for the determination of such metals, owing to the difficulty of ascertaining the end-point of these reactions.

II. Preparation and Standardization of a Dichromate Solution

Method. The potassium dichromate sold by dealers often contains small amounts of potassium sulfate, but can be easily purified by recrystallization. Since the salt is not appreciably hygroscopic an accurately standardized solution can be prepared by weighing out a definite amount, dissolving, and diluting to the proper volume. As the solution is most frequently used for the determination of iron it is convenient to prepare it according to the unitary system, that is, so that 1 cc. will oxidize exactly 0.005 gm. of Fe. As already noted there are a number of factors which affect the method used to determine the end-point of the reaction, and it is always advisable to check the theoretical value of the solution by titrating it against a known weight of a pure ferrous ammonium sulfate under definite conditions.

Detailed Outline of Method. Weigh out exactly 4.39 gm. of the pure salt, dissolve in water and dilute to exactly one liter. Weigh out 1 gm. of pure ferrous ammonium sulfate, dissolve in 100 cc. of water, add 5 cc. of concentrated hydrochloric acid and titrate with the dichromate solution. Use as an indicator a freshly prepared solution of potassium ferricyanide made by dissolving a crystal of the pure salt as large as a grain of wheat in 25 cc. of water. Add at once to the iron solution 26 cc. of the dichromate solution, and then test the mixture for unoxidized iron by bringing a drop of it into contact with a drop of the indicator on a porcelain plate, or piece of glazed white paper. If the test shows an intense blue color continue adding the dichromate solution in quantities of two-tenths of a cubic centimeter at a time

until the test shows a light blue only, then continue adding in quantities of two drops at a time until, after passing thru various shades of blue and green, the tests show a clear yellow only which persists for at least two minutes. Calculate the weight of iron actually oxidized by 1 cc. of the solution.

III. Determination of Iron in Iron Ores

Decomposition. The more easily soluble ores of iron, including siderites, which are mainly ferrous carbonate, and many of the hematites and magnetites, which are mainly ferric oxide and ferrous-ferric oxide respectively, are dissolved by treatment with warm concentrated hydrochloric acid. The action of this acid is greatly intensified by the addition of a small amount of stannous chloride. A small amount of insoluble residue resulting from treatment with these reagents is usually assumed to be free from iron and disregarded, provided it is of a pure white color; it may contain small amounts of iron in the form of an insoluble silicate. Many samples of limonite ores, which contain carbonates and sometimes organic matter, and many ores which contain sulfur, yield to the hydrochloric acid and stannous chloride, only after ignition in an open crucible; this treatment also oxidizes the organic matter, the presence of which might lead to high results.

The more difficultly soluble ores, including many varieties of hematite, magnetite and limonite and all ores containing iron in the form of an insoluble silicate, are most easily and completely decomposed by fusion with sodium peroxide. This treatment yields ferrates and silicates of sodium, also aluminates, chromates and manganates if these elements are present, all of which compounds are easily decomposed by hydrochloric acid. The excess of sodium peroxide used, also the chromates and manganates, are completely reduced by heating with hydrochloric acid and any chlorine which may be liberated is either volatilized or is reduced by the stannous chloride used to reduce the iron.

The action of the molten peroxide of sodium on platinum cru-

cibles is sufficiently energetic to render their use unadvisable; its action on nickel is also appreciable and both nickel and iron, small amounts of which are usually present in the metal of which such crucibles are made, are usually introduced into the resulting solution in sufficient amounts to produce appreciable errors. Crucibles of silver may be used to advantage but well-glazed porcelain ones answer very well, for although the glaze is gradually disintegrated no error is introduced as it does not contain iron, and the crucible can usually be employed for several analyses.

Reduction of Iron by Means of Stannous Chloride. Ferric salts can be reduced by stannous salts as represented by the equation

$$(4) \qquad SnCl_2 + 2\,FeCl_3 \rightarrow SnCl_4 + 2\,FeCl_2.$$

This reaction is almost complete and instantaneous provided the solutions concerned are hot and concentrated, and provided a rather large concentration of hydrochloric acid is also present. Since solutions of ferric salts, especially when hot and when Cl ions are present, possess an intense red or yellow color, whereas solutions of ferrous salts show a slight greenish color only, the point at which sufficient stannous chloride has been added to completely reduce the iron in a solution can be determined with sufficient accuracy by noting the color changes of the solution.

It is scarcely possible to reduce all of the iron in a solution without introducing a slight excess of stannous chloride and since the latter reduces chromic acid, this excess must be oxidized before titration, without at the same time reoxidizing any of the iron. This can be effected by means of mercuric chloride which easily oxidizes the tin but not the iron, and is itself reduced to insoluble mercurous chloride, which compound is not affected by chromic acid. If, however, the solution is hot, and if its concentration with respect to stannous chloride is large as compared with that of the mercuric chloride the reduction may go farther and metallic mercury may be formed, which unlike mercurous chloride is

capable of reducing chromic acid. For this reason care must be taken in using this process to add a slight excess of stannous chloride only, to cool or dilute before adding the mercuric chloride, and to add a relatively large amount of the latter.

Effect of Other Elements on the Process. This method is not affected by the presence of even large amounts of aluminum, manganese, zinc, cadmium, calcium or magnesium. Cobalt and nickel in small amounts are not objectionable, but large amounts affect the accuracy of the end-point. Chromium, in large amounts, increases the difficulty of recognizing the point at which the proper excess of stannous chloride has been added, but in small amounts is not objectionable. Copper, since it is reduced to the cuprous form by stannous chloride and reoxidized to the cupric form by the dichromate, increases the amount of standard solution used almost in proportion to the amount present and also masks the end-point. Antimony and titanium are also reduced by stannous chloride and partly oxidized by the dichromate and hence yield high results. If solutions containing either copper, antimony or titanium are reduced by hydrogen sulfide instead of stannous chloride, correct results can be obtained, since the two first-named elements are precipitated and can be removed by filtration, and the last is not reduced.

Outline of Method for an Easily Soluble Hematite or Magnetite Ore. Weigh out 1 gm. of the finely ground sample into a covered beaker, introduce 20 cc. of concentrated hydrochloric acid and about five drops of stannous chloride solution, cover with a watch glass, and allow to digest on a sand bath until the residue is a pure white color. Rinse the cover and sides of the beaker and transfer the solution to a 100 cc. graduated flask. Cool to room temperature, dilute to exactly 100 cc. and mix thoroughly.

Remove 25 cc. of the solution to a 200 cc. beaker by means of a pipet, add 5 cc. of dilute hydrochloric acid, heat to boiling, and then add stannous chloride solution a drop at a time until the solution is colorless, but carefully avoid adding more than one

drop in excess. Cool the solution slightly, add 50 cc. of water and then 10 cc. of a saturated solution of mercuric chloride. This should produce a white, crystalline, precipitate of mercurous chloride; if it does not do so an insufficient amount of stannous chloride was used; if the precipitate is black or gray too much was used and the results will probably be too high.

Titrate with the dichromate solution as in the standardization, adding it in quantities of 2 cc. until the tests show a change from a deep blue to a light blue, then add the titrating solution until the proper end-point has been reached. With some experience it is possible to obtain a good end-point with the first portion of solution used; beginners usually find it necessary to titrate a second portion, profiting by the experience previously gained. Calculate the per cent of iron present.

Determination of Iron in a Difficultly-soluble Ore. Weigh out into a 20 cc. glazed porcelain crucible approximately 3 gm. of sodium peroxide, avoiding the white crust often found on the surface, which consists largely of sodium carbonate and which, in addition to being less efficient in its action on the ore, has a much higher melting point. Weigh out accurately 1 gm. of the finely powdered ore, add to the crucible and mix with the peroxide with a platinum wire or glass rod. Place the crucible on a gauze, heat slowly until its contents fuse and keep at that temperature for ten minutes; this should produce a clear but deeply colored molten mass.

Allow the crucible to cool, distributing the molten mass over its inner surface by carefully tipping and rotating during solidification. Place the crucible in an evaporating dish, add 50 cc. of water and slowly introduce an excess of hydrochloric acid. Remove and rinse off the crucible, heat the solution to boiling to decompose the hydrogen peroxide formed, then transfer to a 100 cc. graduated flask and treat as in the analysis of easily soluble ores.

The method outlined assumes that neither copper nor any of the other metals which affect the result are present.

IV. Determination of Chromium in Chromite

Theory of the Process. The reaction between a soluble chromate and a ferrous salt can also be used for the determination of the former by using the method of back titration, that is, by adding an excess of a standard solution of ferrous salt and then titrating with a standard dichromate solution. Since all compounds of chromium are readily converted into soluble sodium chromate by fusing with sodium peroxide the method is widely applicable for the determination of this element.

The mineral chromite consists of ferrous oxide combined with the sesquioxide of chromium, but many samples also contain magnesium, aluminum, silicon, and sometimes manganese and nickel. When fused with sodium peroxide, chromates, ferrates, aluminates, silicates and manganates of sodium, also oxide of magnesium and peroxide of nickel, if this element is present or if the fusion is made in a nickel crucible, are produced. The fused mass is readily disintegrated by treatment with water, especially if an excess of peroxide is present. The chromate and most of the silicate and aluminate dissolve readily; the permanganate also dissolves unless an excess of peroxide is present, the ferrate hydrates and forms insoluble ferric oxide or hydroxide; the magnesium and nickel oxides remain insoluble. Hence by digesting the fused mass, filtering off and washing the resulting precipitate a solution which contains all of the chromium as sodium chromate, and no substances which possess strong oxidizing or reducing properties except the excess of sodium peroxide used, is obtained. The peroxide is readily decomposed by heating the solution to boiling. There is evidently no objection to making the fusion in a nickel crucible.

Outline of Method of Procedure. Weigh out about 4 gm. of sodium peroxide, which should not contain much carbonate, into a 30 cc. nickel crucible. Weigh out one-half gram of the finely ground ore, add to the crucible and mix thoroughly with the

peroxide by means of a glass rod. Place the crucible on a wire gauze, heat until the mass fuses to a liquid and keep at this temperature for ten minutes. Decomposition of the sample will be greatly facilitated by seizing the crucible with a pair of tongs and gently rotating the contents. The resulting liquid mass will be of a dark red color and contain much suspended nickel oxide.

Allow the crucible to cool, distributing the contents around the sides during solidification, then place in a capacious evaporating dish and add 100 cc. of water. Heat slowly to boiling and stir until the fused mass is completely disintegrated; remove the crucible from the dish and rinse it off; filter the resulting mixture thru a 11 cm. filter, receiving the filtrate into a 250 cc. graduated flask, and wash until the precipitate is free from soluble chromate. Cool the solution in the flask and dilute to exactly 250 cc.

Measure out 50 cc. of the solution, acidify with hydrochloric acid, and add 5 cc. of the concentrated acid in excess; next add 50 cc. of an approximately one-tenth normal solution of ferrous sulfate, and finally titrate with the standard dichromate solution. Titrate also a second 50 cc. portion of the ferrous sulfate solution directly with the dichromate solution. The difference between the amounts of dichromate solution used in the two titrations corresponds to the chromic acid formed from one-fifth of the ore weighed out. Calculate the percentage of chromium present.

V. Questions and Problems. Series 24

1. In the standardization of a solution of potassium dichromate a solution of a ferrous salt, which has a volume of 100 cc. and contains 0.2 gm. of iron, is used. In titrating an ore with the same solution 0.2 gm. of iron is again present, but the solution has a volume of 600 cc. If the indicator used permits of the recognition of one part of ferrous iron in 100,000, what error results from the fact that the two titrations are made at different volumes?

2. What error might be expected in a determination of iron in an ore containing forty per cent of iron and two-tenths of a per cent of copper, assuming that the copper is completely reduced by the stannous chloride to the cuprous form and reoxidized by the dichromate? *Ans.* 0.17 per cent.

3. Write out all of the reactions involved in the determination of chromium in chromite which contains, in addition to iron and chromium, aluminum, manganese and nickel.

4. Outline an indirect volumetric method for the determination of lead which makes use of a standard solution of potassium dichromate.

5. If a solution of potassium dichromate is one-tenth normal when used as an oxidizing agent, what relation does it bear to normality when used as a precipitating agent?

6. What volume of tenth-normal potassium dichromate would be reduced by 0.1 gm. of iron, (a) when in the form of metallic iron, (b) when in the form of ferrous chloride, (c) when in the form of the magnetic oxide?

7. Why is the oxidizing potential of potassium permanganate greater in an acid than in a neutral solution?

8. How could you decide from the method used for the determination of iron in an ore whether potassium dichromate would oxidize a stannous salt completely?

9. If the equilibrium constant of reaction (2) of page 316 is 0.1, what weights of ferric and ferrous nitrate would be present in a solution which contained 1 gm. of ferric nitrate and had a volume of 479 cc., after an excess of metallic silver had been added? *Ans.* 0.073 and 0.689 gm.

CHAPTER XLVII

DETERMINATIONS WITH IODINE AND SODIUM THIOSULFATE

I. General Features of Iodometric Processes

Typical Reactions. Iodine acts directly as an oxidizing agent by taking up a negative charge and forming the iodine ion as represented by

$$(1) \qquad \overset{++}{Sn} + 2\bar{Cl} + I_2 \rightarrow \overset{++++}{Sn} + 2\bar{Cl} + 2\bar{I}$$

and

$$(2) \qquad 4\overset{+}{Na} + 2\overset{--}{S_2O_3} + I_2 \rightarrow 4\overset{+}{Na} + \overset{--}{S_4O_6} + 2\bar{I},$$

or indirectly, by reacting with water to form both iodine and hydrogen ions and thus rendering the oxygen of the water available as an oxidizing agent, as represented by:

$$(3) \qquad 3\overset{+}{H} + \overset{---}{AsO_3} + I_2 + H_2O \rightarrow 5\overset{+}{H} + \overset{---}{AsO_4} + 2\bar{I}.$$

Of these reactions (1) is practically complete, (2) is complete in a neutral solution and (3) can be made complete in either direction by varying the concentration of hydrogen ion.

In the presence of even small concentrations of a strong base iodine acts very differently since it is itself oxidized to $\bar{I}O_3$ ions as represented by the equation

$$(4) \qquad 6\overset{+}{K} + 6\bar{H}O + 3\,I_2 \rightarrow 6\overset{+}{K} + 5\bar{I} + \bar{I}O_3 + 3\,H_2O.$$

The equilibrium constant of this reaction is small and altho it cannot be made the basis of a quantitative process it often prevents the use of iodine as an oxidizing agent in solutions which contain appreciable concentrations of hydroxyl ions.

The table of electrode potentials on page 320 indicates that the oxidizing potential of iodine is decidedly less than that of permanganates and chromates, and of chlorine and bromine. Experience shows that in the presence of a sufficient concentration of hydrogen ion all of these reagents oxidize the iodine ion to free iodine according to reactions, similar to (5), which are practically complete.

$$(5)\quad 12\,\overset{+}{K} + 2\,\overset{-}{MnO_4} + 10\,\overset{-}{I} + 16\,\overset{+}{H} + 16\,\overset{-}{Cl} \rightarrow 5\,I_2 + 12\,\overset{+}{K} + 16\,\overset{-}{Cl} + 2\,\overset{++}{Mn} + 8\,H_2O.$$

Iodometric Processes. The facts outlined above suggest two classes of reactions which could be used as the basis of volumetric processes. In the first class certain reactions which involve the use of a standard solution of iodine, which acts either directly or indirectly as an oxidizing agent in either a neutral or acid solution, are used for the determination of certain substances commonly classed as reducing agents. Since the degree of oxidation of the iodine in all of these reactions changes from 0 to -1, its oxidizing capacity is always 1. In the second class certain substances, which are usually classed as oxidizing agents, are determined indirectly by causing them to react with an acidified solution of a soluble iodide and titrating the iodine liberated with a solution of a reducing agent. Both classes of processes are included under the term "iodometric."

Preparation of an Iodine Solution. The solubility of iodine in water is too small to make the preparation of even one-tenth normal solutions possible. In the presence of an excess of potassium iodide an unstable but soluble periodide of the formula KI_3 is formed, which, in the presence of reducing agents, decomposes so readily into potassium iodide and free iodine that it can be used as though it were a simple solution of iodine. Solid iodine is readily dissolved by concentrated but not by dilute solutions of potassium iodide and when a solution of the periodide has been

prepared in this manner it can be diluted up to a certain limit without causing free iodine to separate. The solution of iodine in potassium iodide probably contains in addition to normal iodine ions, ions of the formula $\bar{I}_3$.

Preparation of a Standard Reducing Agent. A standard solution of a reducing agent, which reacts completely with the iodine solution can be used to advantage for the readjustment of the standard of this solution, as it is much less stable than potassium permanganate; it is also necessary for processes based upon reactions similar to (5). Sodium thiosulfate is by far the most satisfactory reagent for this purpose, as it is comparatively stable if the solution is kept neutral altho it is slowly decomposed by the carbon dioxide absorbed from the air if left exposed.

Determination of the End-Point. A single drop of one-tenth normal iodine solution imparts an appreciable color to 200 cc. of water and in many of the titrations made with this solution no indicator is necessary. If the solution titrated contains other color-yielding substances, or if greater accuracy is demanded, a solution of starch should be used as an indicator. Under favorable conditions the presence of one part of free iodine in several million can be recognized, by this indicator, but the delicacy of the test and the character of the color produced are affected by a number of factors. It is decidedly less delicate when the concentration of iodine ions and of hydrogen ions is very small. If the concentration of the free iodine present is large as compared with that of the starch, the solution has a green color; if this ratio is smaller it has a blue color; if the solution contains a large concentration of bicarbonates it has a reddish color.

Standardization of the Iodine Solution. The iodine solution can be standardized by titrating against a previously standardized thiosulfate solution, or against a weighed amount of arsenious oxide or potassium antimonyl tartrate (tartar emetic). Owing to the ease with which it can be purified by sublimation the former substance is more generally used.

Since the action of the iodine solution is actually due to the I_3 ions which it contains, the reaction upon which this method of standardization is based is properly represented by the expression

$$(6)\quad 3\overset{+}{H} + \overset{---}{AsO_3} + \overset{+}{K} + \overset{-}{I_3} + H_2O \rightarrow 5\overset{+}{H} + \overset{---}{AsO_4} + \overset{+}{K} + 3\overset{-}{I}.$$

The equilibrium constant for this reaction has been found * to have the value 0.07 at 25° and therefore that

$$(\overset{---}{AsO_4}) \div (\overset{---}{AsO_3}) = (0.07) \cdot (\overset{-}{I_3}) \div (\overset{+}{H})^2 \cdot (\overset{-}{I})^3.$$

The only factor which can be varied for the purpose of displacing the equilibrium in the desired direction and making the ratio $(\overset{---}{AsO_4}) \div (\overset{---}{AsO_3})$ very large is $(\overset{+}{H})$. Evidently $(\overset{+}{H})$ must be made small as compared with 0.07 if the oxidation of all the arsenic present is to be made reasonably complete when an equivalent amount of iodine solution has been added. Since hydrogen ions are formed as the reaction progresses it is also necessary to introduce some reagent, like sodium bicarbonate, which will keep the concentration of hydrogen ions small and which does not yield sufficient concentrations of hydroxyl ions to cause reaction (4) to take place. Experience has shown that the proper conditions are maintained if the solution has a volume of 75 cc., if it is made neutral to phenolphthalein and if 2.5 gm. of pure sodium bicarbonate is added and the solution saturated with carbon dioxide.

II. Classification of Iodometric Processes

Determination of Substances Oxidized by Iodine. Under this head are included the element tin, which is oxidized from the bi- to the quadrivalent condition even in the presence of acids, and arsenic and antimony, which are oxidized from the tri- to the quinquivalent condition under the conditions noted in the preceding paragraph. Under the same head are included sulfurous acid which is oxidized to sulfuric acid in neutral or acid solutions;

* Washburn, Jour. of Am. Chem. Soc., **30**, 31 (1908).

hydrogen sulfide, which is oxidized to sulfur and hydriodic acid under similar conditions; thiosulfuric acid, which is oxidized to tetrathionic acid (see reaction 2) under similar conditions; and salts of hydrocyanic acid, which are oxidized to cyanogen iodide and a salt of hydriodic acid in a neutral solution.

Determination of Substances Reduced by Hydriodic Acid. Three factors can be varied for the purpose of making reactions similar to (5) sufficiently complete and rapid to make the determination of oxidizing agents possible. First, a large amount of a soluble iodide may be added for the purpose of making the concentration of the iodide ions large. Thus the reaction in which the ferric ion is reduced may be made complete to such an extent as to make it useful in the determination of ferric salts by the use of a large excess of potassium iodide.

Second, the concentration of the hydrogen ion can be made large by the addition of a strong acid. Thus altho chlorine and bromine are completely reduced by moderate concentrations of soluble iodides, cupric salts, also permanganates and chromates, are not completely reduced unless a small concentration of hydrogen ion is also present and arsenates and antimonates are not completely reduced unless this concentration is very large.

Third, by increasing the temperature to the boiling point of the solution the iodine formed is volatilized and the equilibrium forced in the desired direction. Such determinations are necessarily carried out in a distilling apparatus, in which all of the iodine formed is distilled into a receiver before being titrated. This device has been successfully used in the determination of molybdenum which can be reduced from the hexa- to the trivalent condition.

Indirect Iodometric Determinations. A number of insoluble oxidizing agents, such as the peroxides of manganese and lead, are completely reduced by concentrated hydrochloric acid at moderately high temperatures and the chlorine produced can be distilled into a solution of potassium iodide, and the resulting

iodine titrated. This forms the basis of an indirect method for the determination of these oxides and in general of all oxidizing agents which are completely reduced under these conditions.

A second series of indirect processes represents combinations of precipitation and oxidation processes. As already noted chromic acid and its salts can be determined by reducing with potassium iodide and titrating the resulting iodine; hence those metals which form insoluble chromates can be determined by adding a measured volume of a standard solution of a soluble chromate, filtering off the precipitate formed and determining the soluble chromate left in the filtrate; the amount of metal present can then be calculated from the difference between the soluble chromate added and that found in the filtrate.

III. Outline of Method for Preparation of Solution

Preparation of Iodine Solution. Weigh out 12.7 gm. of pure iodine, place in a small beaker, add 20 gm. of potassium iodide and 20 cc. of water and stir occasionally until the iodine is completely dissolved. Dilute the mixture slowly to one liter and place in a clean bottle made of colored glass or one which is covered with opaque paper.

Preparation of Starch Solution. Place about a gram of starch in a small beaker, add about 20 cc. of water and stir until the mixture is smooth. Heat in a separate beaker 200 cc. of water to boiling, pour the starch mixture into it and boil the resulting mixture for three minutes, being careful to prevent any of the starch from settling to the bottom, for if it does so the beaker will crack. Allow the mixture to stand for several hours, then decant off the clear portion.

Standardization of Iodine Solutions. Weigh out 0.2 gm. of pure arsenious oxide, dissolve in 20 cc. of an approximately normal solution of sodium hydroxide, add a drop of phenolphthalein and then dilute hydrochloric acid until the solution is just colorless. Dilute the solution to 75 cc., add 2.5 gm. of sodium bicarbonate,

and pass carbon dioxide thru it until saturated. Add about 1 cc. of the starch solution, and titrate with the iodide solution added from a glass-stoppered buret until the mixture acquires a faint but permanent rose to purple color. Calculate the relation of the solution to normal strength, assuming that the reducing power of the arsenious oxide is four.

Preparation of Thiosulfate Solution. Weigh out 24.8 gm. of pure crystallized sodium thiosulfate ($Na_2S_2O_3 \cdot 5\,H_2O$), dissolve and dilute to one liter. Measure out by means of a pipet 25 cc. of the iodine solution, dilute to 75 cc. and titrate with the thiosulfate solution. It will be found desirable to add the latter until the mixture has a very faint yellow color before adding the starch indicator and then to continue the titration until the mixture changes from blue to colorless. Calculate the relation which the thiosulfate solution bears to normal strength.

IV. Determination of Arsenic in Paris Green

Composition of Sample. Paris green is an aceto-arsenite of copper which is largely used in combating insects injurious to cultivated plants. The composition of commercial samples varies and one of the factors which determine their value for the purpose indicated is the percentage of arsenic present.

Theory of Method Used. Arsenic can be determined by oxidizing it from the tri- to the quinquivalent condition with a standard solution of iodine, or by reducing it from the quinquivalent to the trivalent condition by means of hydriodic acid and titrating the liberated iodine with a solution of sodium thiosulfate. When Paris green is treated with a solution of sodium hydroxide, cuprous oxide, sodium acetate, and a mixture of sodium arsenite and sodium arsenate are produced. The insoluble cuprous oxide can be filtered off and the arsenic determined in the filtrate by reducing it to the trivalent condition with hydriodic acid in a strongly acidified solution, reducing the liberated iodine, neutralizing the solution and titrating with an iodine solution.

Outline of Method of Procedure. Weigh out 2 gm. of the sample into a small beaker, add 25 cc. of 2-normal solution of sodium hydroxide, heat cautiously for some five minutes or until converted into bright red cuprous oxide. Rinse the mixture into a 100 cc. graduated flask, cool and dilute to exactly 100 cc. and then filter thru a dry filter, rejecting the first 10 cc. of filtrate. Remove 25 cc. of the filtrate to a 300 cc. beaker, add 15 cc. of concentrated hydrochloric acid and 2 gm. of potassium iodide and then add one-tenth normal sodium thiosulfate solution until the mixture is just colorless. As the volume is small it is not necessary to use an indicator. Next add 40 cc. of water and one drop of phenolphthalein, then add slowly a 20 per cent solution of sodium hydroxide until the mixture shows a faint pink color. Acidify with a drop of dilute hydrochloric acid, add 2.5 gm. of sodium bicarbonate, saturate with carbon dioxide and titrate with iodine solution as in the standardization. Calculate the percentage of As_2O_3 present.

V. Determination of Copper in Brass

Theory of Method. All soluble cupric salts react with potassium iodide in neutral or slightly acid solutions as represented by

$$2\,CuSO_4 + 4\,KI \rightarrow 2\,CuI + 2\,K_2SO_4 + I_2. \qquad (7)$$

The fact that cuprous iodide is very insoluble and that cupric iodide is very unstable gives the equilibrium constant of this reaction a large value. The most favorable conditions are the presence of from 3 to 5 per cent of potassium iodide and about 3 per cent by volume of concentrated hydrochloric acid. With a smaller concentration of hydrogen ion the reaction is slower and the endpoints less distinct. The presence of large concentrations of soluble salts especially of acetates seem to retard the reaction; the reason for this is not apparent.

When brass is dissolved in nitric acid small amounts of nitrous acid are produced; as this reagent slowly liberates iodine from

potassium iodide it must be expelled by evaporation or oxidized by bromine or hydrogen peroxide before making the titration.

Outline of Method of Procedure. Weigh out 0.3 gm. of sample into a 200 cc. beaker, add 10 cc. of dilute nitric acid, cover with a watch glass and warm gently until the metal dissolves. Remove the cover, rinse its under side with water and evaporate the solution to about 3 cc. Dissolve basic salts if such have separated with a few drops of nitric acid and dilute to 50 cc. Add sufficient ammonium hydroxide to produce a clear bright blue solution, then neutralize with hydrochloric acid and add 3 cc. of the dilute acid in excess.

Cool the solution to 25°, add 3 gm. of potassium iodide and stir until dissolved. Titrate with the thiosulfate solution until the mixture has a light yellow color only, then add starch solution and continue the titration until the light blue or lilac color of the mixture fades to a nearly pure white and does not regain a perceptible blue color after three minutes. Calculate the percentage of copper present.

VI. Determination of Copper in a Chalcopyrite Ore

Interfering Elements. These ores usually contain in addition to copper and iron sulfides small amounts of lead, zinc and arsenic sulfides. When dissolved in nitric acid the iron is oxidized to the trivalent and the arsenic to the quinquivalent condition. As both elements are reduced by hydriodic acid it is necessary to separate the copper before using this method. Small amounts of lead and even large amounts of zinc have no effect upon the process.

Separation of Copper by Metallic Aluminum. The oxidizing potential of cupric salts is large as compared with that of metals like zinc, magnesium and aluminum, and under certain conditions it is possible to separate copper from such solutions completely by means of these metals. Aluminum is to be preferred for this purpose owing to the slowness with which it is attacked by moderately

strong solutions of sulfuric acid. The separation of copper by this metal is retarded by ferric iron, which is reduced to the ferrous condition before the copper begins to separate. It is rendered incomplete by the presence of even small concentrations of nitric acid. It is most rapid when the solution is kept hot and enough sulfuric acid is present to cause the formation of sufficient hydrogen to stir the solution vigorously. Under these conditions all of the copper, most of the lead and a part of the arsenic but none of the zinc and iron are precipitated. The small amount of arsenic which may separate with the copper does not affect the final titration appreciably if the solution is acidified with acetic instead of hydrochloric acid.

Outline of Method of Procedure. Weigh out 1 gm. of the ore into a 200 cc. Erlenmeyer flask, add 5 cc. of concentrated nitric acid and warm until violent action is over, next add 10 cc. of concentrated hydrochloric acid and evaporate until the volume has been reduced to one-half, then cool, add very cautiously 8 cc. of concentrated sulfuric acid, and evaporate until the flask is filled with dense white fumes of sulfur trioxide. Cool the flask, add 30 cc. of water and allow to stand with occasional shaking until all the soluble salts have been brought into solution. Transfer the solution to a 200 cc. beaker, retaining the insoluble matter as far as possible in the flask but washing the latter thoroughly; the final volume should not exceed 70 cc.

Add to the solution a strip of aluminum foil 3 cm. wide and 15 cm. long, which has been bent into the form of the letter S, heat to 80° and set aside in a warm place until the copper has been completely precipitated, which usually requires ten minutes more than the time necessary to decolorize the solution. Next add 10 cc. of water saturated with hydrogen sulfide, and if the solution remains colorless or acquires a faint brown coloration only filter at once, using a small filter and retaining as much of the precipitated copper in the beaker as possible. Wash the precipitate three times with 10 cc. portions of hydrogen sulfide.

Place the beaker containing the precipitate under the funnel and pour over the filter about 10 cc. of warm dilute nitric acid, moving the beaker in such a manner as to cause the acid solution to flow over the surface of the aluminum plate and dissolve the small amount of adhering precipitate. Replace the beaker by the flask used to dissolve the ore which has in the meantime been cleaned. Warm the solution in the beaker until all of the precipitate has been dissolved, then remove and rinse the aluminum plate, pour the solution thru the filter and wash free from copper.

Add 10 cc. of bromine water to the flask and boil vigorously until the excess added is expelled. Cool the solution, make alkaline with ammonium hydroxide, acidify with acetic acid and then add 3 cc. of the dilute acid in excess. The solution should have a volume not greatly exceeding 60 cc.

Add 3 gm. of potassium iodide and titrate as in the previous determination, remembering that slightly more time must be allowed for the mixture to come to equilibrium owing to the smaller concentration of hydrogen ion present.

VII. Questions and Problems. Series 25

1. A solution contains 0.1 gm. of H_3AsO_4 and 1 gm. of HCl, and has a volume of 100 cc.; if 3 gm. of potassium iodide is added and it is assumed that the potassium iodide and the three acids are completely dissociated, what fraction (calculated approximately) of the H_3AsO_4 is reduced?

Ans. 0.6.

2. Write out all of the reactions involved in the determination of arsenic in Paris green.

3. Outline the changes resulting from the addition to water of (a) Na_2CO_3, (b) $NaHCO_3$, (c) $NaHCO_3 + CO_2$. What other reagents could be substituted for $NaHCO_3$ in the standardization of the iodine solution?

4. Show how you could standardize a solution of iodine from a standard solution of (a) $KMnO_4$, (b) $K_2Cr_2O_7$.

SECTION X

PHYSICO-CHEMICAL PROCESSES

CHAPTER XLVIII

THEORY OF PHYSICO-CHEMICAL METHODS

Uses of Physical Constants. The analyst often finds it desirable to determine certain physical constants of substances submitted to him, usually with one of three objects in view. First, for the purpose of identifying or characterizing such substances. Use is here made of the well-established principle that the physical constants of every pure substance are definite magnitudes, whose values are often changed materially by the presence of small amounts of impurities; the extended uses made of the melting-points of solids and of the boiling-points of liquids for this purpose are good illustrations. Second, to determine whether the com-
n of the substance lies within the limits which characterize
tances to which it is supposed to belong; especially
of adulterations in certain food products, or other
ural origin, which are complex mixtures. Third,
tion of the percentage composition of certain
n be analyzed by such methods more easily or
n by methods which are purely chemical.

tures With Additive Properties. The quanti-
nixtures by physico-chemical methods involves
rement of some physical property of the sample,
of this result with the corresponding physical
pure components of the mixture, or with a series

of constants representing similar mixtures of known composition. If the sample is a simple mechanical mixture of two components an additive relation may exist between certain of its physical constants and those of the two components, that is, $\frac{dE}{dP}$ is a constant where dE and dP represent correlated changes in the constant concerned, and the percentage of one of the constituents in the mixture. In some cases the expression has a constant value only when P represents the relation between the number of molecules, of one constituent and the total number of molecules in the mixture; in other cases it is constant when P represents concentration, that is, the weight of one constituent per unit volume of mixture.

If the constant found for such a mixture is represented by E, and the corresponding constants of its two components A and B are represented by E_1 and E_2, the additive relationship would require that $xE_1 + (100 - x)\,E_2 = 100\,E$ where x and $(100 - x)$ represent the percentages of A and B respectively. The value of x can then be easily calculated by the use of the derived formula

$$x = \frac{100\,(E - E_2)}{E_1 - E_2}.$$

The accuracy of such a process clearly depends, not only upon the accuracy with which the three constants E, E_1 and E_2 are determined, but also upon the value $(E_1 - E_2)$.

Such methods cannot be used for the analysis of mixtures containing more than two components unless one or more of the components is without effect upon the property concerned. Theoretically it is possible to analyze a mixture containing three components by measuring two of its physical constants, formulating two equations similar to that already given, and solving these in the customary manner.

Mixtures Whose Properties Are Not Additive. Mixtures which possess purely additive properties are rare, altho the de-

partures from pure additive relationships are not infrequently so small that they can be disregarded.

Considering first solid mixtures, three types of structural units are possible. First, the two substances may themselves exist as distinct independent structural units; second, they may form one or more series of solid solutions with each other, each with definite saturation limits; and third, they may form one or more chemical compounds, often when the appearance of the mixture gives no evidence of chemical changes having taken place. Mixed types are also possible, that is, the pure components may form solid solutions with the compounds and the compounds may form solid solutions with each other.

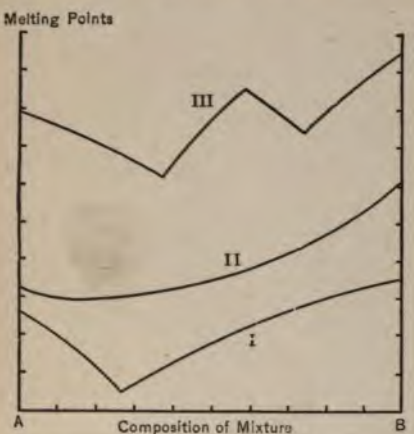

Fig. 62. — Melting Points of Mixtures of Two Solids

The significance of these three types of structure in the interpretation of the physical constants of mixtures is illustrated by the curves shown in Fig. 62. The abscissas here represent the relative amounts of the two components A and B in the mixture, and the ordinates the temperatures at which they begin to solidify when cooled from the molten condition. Curve I illustrates mixtures which form neither solid solutions nor compounds, and is characterized by a distinct break, which represents the so-called eutectic point. Curve II illustrates mixtures which form a continuous series of solid solutions; it is characterized by a minimum, altho certain mixtures of this type show a maximum. Curve III illustrates mixtures which form a single stable compound; it shows a well-defined cusp at the point which represents the composition

of the compound. The corresponding curves for mixtures which show mixed types of structure are still more complex, but can be easily interpreted from the relations found in the simpler cases.

The factors which affect the physical properties of liquid mixtures are the possible association of the molecules of the solvent, the formation of molecular complexes, especially hydrates and double salts, and the electrolytic dissociation of the solute. The relations are decidedly simpler than where solid mixtures are concerned, and the curves representing many of the physical constants of liquid mixtures, especially where there is no dissociation, or where the dissociation is nearly complete, are straight or slightly curved lines.

Use of Interpolation Methods. In all cases in which the constant measured is not an additive function of its two components, it becomes necessary to measure this property for a sufficient number of mixtures containing known proportions of these components before it can be used for the analysis of unknown mixtures. The composition of the unknown mixture is then determined by interpolating the value found between the proper interval in the table which has been prepared. If the relation made use of is represented by a curve which shows a maximum or a minimum, certain of the determinations made may correspond to two different points on it, and therefore to either of two mixtures whose percentage composition may differ greatly. If the mixture is a solid this is a serious difficulty, but if it is a liquid the composition of the mixture under examination can be inferred from the effect produced upon the constant by increasing the dilution. If the curve shows a maximum, and increasing the dilution increases the value of the constant employed, the mixture represents the more concentrated of the two in question; if it shows a minimum the reverse relationship must hold.

The error involved in the interpolation depends upon the form of the curve at different intervals; the most favorable condition is where the curve forms an angle of 45° with the horizontal axis.

Physical Constants Most Largely Used. The physical constants largely used for quantitative determinations are the specific gravity, specific volume, colorific absorption, index of refraction, and optical activity. A number of others, such as the conductivity for electrical energy, are used more rarely. The three first named will be considered in detail in the subsequent chapters.

Index of Refraction. This is defined as the ratio of the sine of the angle of incidence to that of the angle of refraction, when a beam of light passes from air to a layer of the medium under consideration. It is used especially for the analysis of liquid solutions. The refractometer devised by Abbé is largely used for such determinations; it is based upon the measurement of the angle at which an incident beam of light is totally reflected when it passes thru a double prism which is made of glass but has the form of a Nicol prism. The determination consists in placing a drop of the liquid between the two parts of the prism and rotating its position in a vertical plane until a shadow is cast at a particular position, that is, corresponds to the cross-bar of a telescope, with which the instrument is provided. The angle thru which the prism is turned is read on a scale by means of a magnifying glass in terms of refraction index directly. It can be used for liquids varying from 1.3 to 1.7 with a maximum error which is less than 1 in the third decimal place. This instrument is used especially for the examination of fats and oils and was found especially satisfactory for the detection of adulterants in olive oil and butter.

The instrument of Zeiss is based on the same principle, altho the mechanical construction and method of making the measurement are totally different. The single glass prism used is immersed in a small beaker containing the liquid to be tested, and the observed results are expressed on an arbitrary scale, which corresponds to a range in refractive index of from 1.325 to 1.366.

The refractive indices of aqueous solutions of a large number of organic and inorganic compounds have been found to bear a simple relation to their concentration, and the percentage com-

position of a large number of such solutions can be determined with the aid of the tables showing this relation. It is possible to analyze by this method certain mixtures which are extremely difficult to analyze by any other method. Mixtures of methyl and ethyl alcohol are good illustrations. The curves representing the refraction indices of aqueous solutions of these compounds show the wide divergence represented in Fig. 63. It so happens that the specific gravities of aqueous solutions of the two alcohols of the same percentage composition are nearly equal, and that of mixtures correspond to the sum of the percentages of the two alcohols present. Hence the percentage composition of such mixtures can be determined by comparing the sum of the two percentages, which is ascertained from a specific gravity determination, with the difference between the refractive indices of aqueous solutions of the two alcohols corresponding to this percentage. The accuracy of the method is evidently at a maximum when the divergence between the two curves is greatest, that is, when the sum of the two percentages exceeds ninety. The uses of the refractometer in quantitative work are extremely varied and important.*

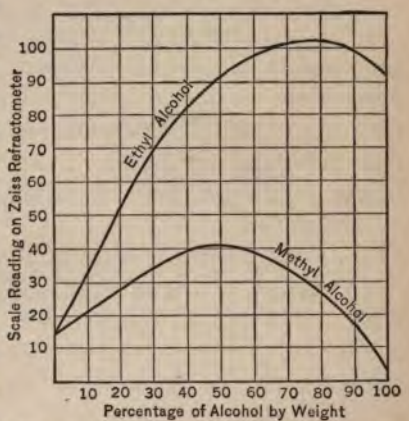

Fig. 63. — Refractive Index of Solutions of Methyl and of Ethyl Alcohol

Specific Rotary Power. The ability to rotate the plane of a beam of polarized light is possessed by a very few solid substances, by a limited number of organic liquids, and by solutions of those organic compounds which contain an asymmetric carbon atom,

* See Lythgoe, Report of the Eighth International Congress of Applied Chemistry, Vol. I, p. 295 (1912).

that is, an atom which is directly linked with four different elements or radicals. In some cases the plane is turned to the right and in others to the left, and the magnitude of the effect is one of the specific constants of all such substances if the comparison is made under identical conditions. It can be measured by means of a polariscope, of which a large number of different forms are in use. These instruments consist of two Nicol prisms mounted in the same horizontal axis, between which a tube of known length filled with the liquid under examination is placed. The angle thru which one of the Nicols must be rotated to compensate for the rotation of the liquid, or the thickness of a piece of optically active quartz necessary to compensate for it is measured by a variety of optical devices.

The optical activity of solutions is directly proportional to the concentration of the solution and the length of the column thru which the polarized beam passes. Hence the percentage composition of any solution can be calculated from its optical activity, if the activity of one solution containing a known concentration of the substance concerned is known. Further, the scale of the polariscope used can be so marked as to give directly the percentage of any one desired substance, provided the solution of the sample used is made to contain a specified concentration of the sample and examined in a tube of specified length.

One decided advantage of making use of the optical activity of solutions for quantitative work is that the number of substances which produce this effect are so limited, and the determination of those substances which do possess it is not effected by the impurities usually present. It is especially useful in the determination of the different sugars, and related substances, and the identification of the different terpenes and essential oils. The subject is a very large one and cannot be considered in detail here.*

* See Browne, Handbook of Sugar Analysis.

CHAPTER XLIX

PROCESSES BASED UPON THE DETERMINATION OF THE SPECIFIC GRAVITY OR SPECIFIC VOLUME OF SOLIDS OR LIQUIDS

I. General Features of the Methods

Definition of Specific Gravity and Specific Volume. The "specific gravity" of solids and liquids is defined as the ratio between a mass of the substance concerned, and that of an equal volume of water. The relation thus defined is not a definite one unless the temperatures at which both the measurements concerned have been made are also specified. A temperature of 4° is usually adopted for the measurement of the standard water volume, but it is customary to adopt a more convenient one, especially 15°, 20° or 25°, in measuring the volume of the substance compared with it. The temperatures actually used are conveniently expressed in the form of a fraction; that is, $\left(\frac{20°}{15°}\right)$ C. is used to express the fact that the water was measured at 15° C., and the substance concerned at 20° C.

The specific gravity of substances referred to water at any specified temperature can be converted into the equivalent value referred to water at 4° C. by multiplying by the specific gravity of water at the specified temperature.

Corrections for the buoyant effect of the air upon the masses determined, and for the expansion of glass vessels used thru temperature changes, are not necessary unless results of extreme accuracy are demanded.

The "specific volume" of solids and liquids is the reciprocal of

the specific gravity; that is, it is the volume occupied by the solid or liquid, as compared with the volume occupied by an equal mass of water.

Methods of Determining the Specific Gravity of Solids. The chief difficulty encountered in determining the specific gravity of a solid is to devise a method by which its volume can be determined with sufficient accuracy. It is usually determined by measuring the buoyant effect which some liquid, whose specific gravity is known, has upon it. The method of procedure is represented in Fig. 64. The object A is suspended in the liquid from the arm of a balance by means of a piece of aluminum wire, and the weight necessary to counterbalance it ascertained. This result is then corrected by determining and subtracting the weight necessary to counterbalance the wire used, when immersed to the same depth. The difference between the weight of the object in air w and the weight in the liquid w_1 represents the weight of liquid displaced, and this difference divided by the specific gravity of the liquid used, its volume. If G represents this specific gravity, that of the solid can be calculated from the formula

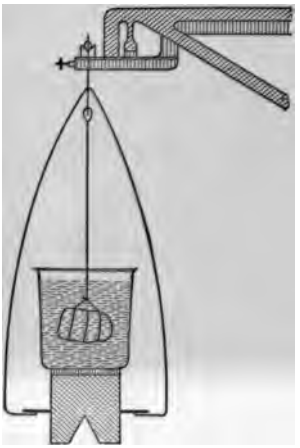

Fig. 64. — Apparatus for Determination of Specific Gravity of Solids

$$\text{Sp. Gr.} = \left(\frac{w}{w - w_1}\right) G.$$

The liquid most frequently employed is water, and in this case G has the value one if the unit of volume to which the specific gravity is to be referred is that of water at the temperature used. If the solid is dissolved or acted upon chemically by water some other liquid must be used.

In using this method large errors may arise from small bubbles of air which adhere to the immersed sample or to the wire, or are retained in the cracks or crevices often found in solid mixtures. This difficulty can be avoided by placing the vessel containing the immersed sample under a bell jar and exhausting the air, or by boiling the liquid surrounding the sample until all the air has been expelled. The error in determining the volume is always greater than that involved in determining the weight because the movement of the balance beam is greatly hampered by the resistance against the movement of the immersed solid presented by the liquid.

Fig. 65.—Pycnometer

If the solid consists of small masses another method must be used. One of these is based upon the use of a "pycnometer" flask similar to that represented in Fig. 65. This consists of a small bottle, which is provided with a carefully-fitted glass stopper, pierced by a capillary opening and therefore capable of containing a definite volume when filled to some particular mark on the capillary. The weight w_1 of some liquid, whose specific gravity G is known, which is contained by the flask when filled to the mark is first determined; a known weight w of the sample is then introduced, the level of the liquid again brought to the mark, and the weight w_2 of the contents of the flask again determined. The volume displaced by the sample must equal $(w + w^1 - w^2) \div G$ and the specific gravity is calculated from the formula

$$\text{Sp. Gr.} = \left[\frac{w}{w + w^1 - w^2}\right] G.$$

Direct Determination of the Specific Gravity of Liquids. The specific gravity of liquids can be determined more readily and more accurately than that of solids. The relative masses of equal volumes of the liquid concerned, and of water, can be determined

directly by means of a pycnometer flask, or still more accurately by the Ostwald-Sprengel tube represented in Fig. 67. This tube is successively sucked full of the desired liquids, until one capillary is completely filled and the other is filled to the indicated mark, and then accurately weighed. The accuracy of the result obtained with this device can be increased to almost any desired degree by using tubes of sufficient capacity, and using the proper precautions in filling and weighing. An error of one in the fourth decimal place need not be exceeded if the capacity of the tube is at least 10 cc.

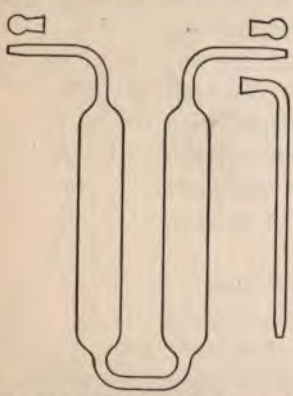

Fig. 66. — Ostwald-Sprengel Tube

The Use of Hydrometers. Where speed is of more importance than accuracy, the specific gravity of liquids is frequently determined by means of a hydrometer. This instrument consists of a spindle-shaped float, which supports a narrow cylindrical stem bearing a graduated scale as represented in Fig. 67. When placed in a liquid such a float must displace its own weight of the liquid conned, and hence the point on the stem to which it sinks st depend upon its weight, and the specific gravity he solution. It can be calibrated by placing it in a s of liquids of known composition, or specific grav- and marking the points to which it sinks on the e attached to the stem. It should be noted that al changes in the specific gravity of the solutions used do not the points to which it sinks by equal increments. If the which it displaces in a liquid which has a specific gravity represented by a the weight of the hydrometer must be the volumes displaced when placed in liquids having

Fig. 67.— Hydrometer

specific gravities of 1.01, 1.02 and 1.03 respectively would be $1 \times a$ divided by these numbers. Since the three quotients do not differ from each other by equal amounts, it is evident that each division on the scale, corresponding to an equal difference in specific gravity, must have a slightly different value.

The sensitiveness of the hydrometer, that is, the change in the point to which it sinks resulting from a given change in specific gravity, depends upon the ratio between the volume displaced in pure water, and the volume displaced by a unit length of the stem. Hydrometers of any desired degree of delicacy can be constructed by varying the relative size of the immersed bulb, as compared with the diameter of the stem. Increasing the sensitiveness by this means necessarily decreases the range of specific gravities for which it can be used, unless the stem is prolonged to a point which not only renders the instrument cumbersome and easily broken, but necessitates the use of a large amount of liquid for a determination. Hence for the accurate determination of specific gravities ranging from 0.7 to 2, which includes the usual range of possibilities, a number of instruments, each one of which covers a part of this interval, are necessary. A set of eighteen such instruments, each of which has a displacement of about 12 cm. and a stem 5 mm. in diameter, makes it possible to determine specific gravities over this range to the third decimal place. In such a set the ratio of the volume displaced, when in water, to the volume displaced by that interval on the stem which corresponds to one scale division is large, and the scale divisions for each hydrometer of the set can be made uniform without introducing very large errors.

One source of error in the use of hydrometers is the result of the surface tension exerted by the liquid on the stem which tends to increase its displacement. As a consequence a hydrometer will show a slightly different reading when placed in two liquids which have the same specific gravity but different surface tensions. Fortunately these differences are small.

The Calibration of Hydrometers. Although hydrometers can be calibrated to show specific gravity referred to water at 4°, or to any desired unit of volume, their widespread use for certain technical purposes has led to the employment of a number of empirical and arbitrary scales, some of which have but little to recommend them.

If the result ultimately desired is the percentage composition of a solution of some one substance, it is obviously rational to calibrate the hydrometer used to read percentages of that substance directly. Hence a number of "direct percentage" hydrometers which give directly the percentage of alcohol (alcoholometers), of sugar (saccharometers), of urea (ureometers), etc., in aqueous solutions are in use. They are of but little use, except for the analysis of one particular kind of solution.

A number of the hydrometers first used in analytical work were calibrated so that the volume displaced by that part of the stem corresponding to one scale division bore a very simple numerical relation to the volume displaced when in water. This relation can not be regarded as a true constant unless the scale divisions differ by small values; it is known as the "modulus" of the hydrometer. Thus the modulus of the Gay-Lussac hydrometer is 100, that of the Balling 200, and that of the Brix 400.

The Baumé hydrometer was originally calibrated by marking the point to which it sank in water 0 and in a 10 per cent salt solution 10, and continuing the same scale units down the stem. Somewhat later its use in factories manufacturing sulfuric acid became general, and it was found convenient to standardize it by marking the point to which it sank in sulfuric acid, which had a specific gravity of 1.842, 66. The two methods of calibration agree with a fair degree of approximation only, and since different
tries have adopted different temperatures for the calibration
lue of a Baumé degree is an uncertain quantity. The
hydrometer was also adapted for use with liquids lighter
by marking the point to which it sank in pure water 10

and in a 10 per cent salt solution 0, and continuing the same scale units up the stem.

The Twaddle hydrometer is calibrated so that each unit represents five units of specific gravity in the third decimal place, that is, 9° Twaddle = 1.045 Sp. Gr.

All hydrometers are calibrated for use at some definite temperature, which should be specified on the label with which they are provided. Many of them also carry a small thermometer, which obviates the need of a second instrument.

Calculation of Specific Gravity from any Hydrometer Scale. The analyst is often obliged to calculate specific gravity from any of the arbitrary scales with which a hydrometer may be provided, or to convert specific gravities into such scale readings. This can be easily effected if the modulus of the instrument concerned is known. Thus the modulus of the American Baumé hydrometer, which is calibrated for $(\frac{60}{60})$ Fahrenheit, is 145. This means that the volume displaced by it when floating in pure water is 145 times as great as the volume displaced by that portion of the stem representing one scale division. Hence the volume displaced when immersed in a liquid of specific gravity x must be $(145 \div x)$ times this unit and the change in the point to which it sinks must be represented by $145 - (145 \div x)$. Therefore

$$\text{Degrees Baumé (for heavy liquids)} = 145 - \frac{145}{\text{sp. gr.}} \text{ at} \left(\frac{60}{60}\right) \text{F°}.$$

The Baumé hydrometer for liquids lighter than water has a modulus of 140 and the point to which it sinks in water is marked 10, hence the corresponding formula is:

$$\text{Degrees Baumé (for light liquids)} = \frac{140}{\text{sp. gr.}} - 130 \text{ at} \left(\frac{60}{60}\right) \text{F°}.$$

The corresponding formulæ for the Gay-Lussac, the Balling and the Brix hydrometers differ from that given above only in that the numbers 100, 200 and 400, respectively are substituted for 145.

The Westphal Balance. The specific gravity of liquids can also be calculated from the buoyant effect which they exert when

solid objects of known mass and volume are immersed in them. A device which makes use of this principle is the Westphal balance, which is represented in Fig. 68. It consists of a light metal beam suspended horizontally. One end of the beam is provided with a pointer, which indicates its position with reference to a second pointer attached to the frame supporting the beam, and a knob whose weight is sufficient to counterbalance a glass plummet suspended from the other end of the beam. If the plummet is completely immersed in a liquid the latter exerts a buoyant effect, which is determined by the product of two factors, namely, the specific gravity of the liquid and the volume displaced by the plummet. This effect can be measured by ascertaining what weight must be added to the end of the beam from which the plummet is suspended to cause the beam to assume a horizontal position.

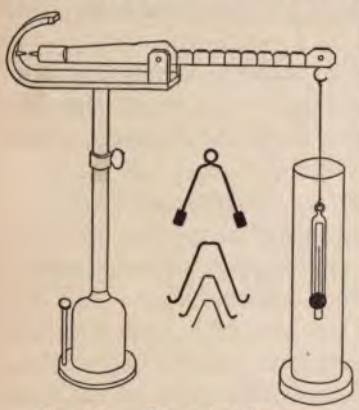

Fig. 68. — Westphal balance

If the unit of weight employed in making this measurement corresponds exactly to the buoyant effect which is found when the plummet is immersed in water, the weights, measured in terms of this unit, found to be necessary when the plummet is immersed in any other liquid, give at once the specific gravity of that liquid. Hence the apparatus is provided with a special set of weights, made to take the form of riders, which bear simple relations to the volume and weight of the plummet. Since that half of the beam from which the plummet is suspended is divided into ten equal divisions, only five such weights, two of unit value and one each of 0.1, 0.01 and 0.001 of this value are needed to counterbalance the buoyant effect of any liquid mixture, whose specific gravity ranges from 1.001 to 2.999.

The specific gravity of liquids can be determined with this instrument in a few minutes, often with an error not exceeding 0.0005. The error involved increases rapidly with the viscosity of the liquid concerned, owing to its action on the movements of the plummet, which prevents the beam from attaining its normal position.

Analysis of Solid Mixtures. The specific volume of a solid mixture is a simple additive function of the specific volumes of its components if the mixture represents a simple conglomerate. This statement is also approximately true of mixtures which consist of solid solutions. Altho theoretically this principle is applicable to the analysis of all heavy mixtures of either of these classes, the number of cases in which it can be used with a sufficient degree of certainty and accuracy is small. It is often difficult to ascertain whether small amounts of other components are not also present; this is especially true of naturally occurring substances, which often contain solid or liquid inclusions, which can only be recognized by making a thin section and examining it with a compound microscope. The specific volume of many solids is affected by the rate at which they have been cooled during solidification; that of other solids, especially metals and alloys, is affected by mechanical deformation, such as hammering or rolling. Still others can exist in two or more allotropic forms which differ in specific volume and which may persist above or below the normal temperature limits at which they are stable. The most important applications of the method are in determining the relative amounts of two minerals in a rock formation and in the analysis of certain simple alloys.

Analysis of Liquid Mixtures. The most widely used of all physico-chemical methods are determinations of the percentage composition of aqueous solutions by means of specific gravity determinations. They cannot be used where the liquid mixture contains appreciable amounts of a third constituent, for every component of such mixtures has some effect upon its specific

gravity. Even when two components only are present the specific gravity of such mixtures rarely bears a simple relation to those of the pure components, at least over a wide range of concentrations. The simplicity and accuracy with which specific gravity determinations can be made has led to the preparation of a large number of tables which give this relation for a great variety of such mixtures, and has resulted in their extended use in many kinds of technical work.

II. Analysis of a Lead-Tin Alloy

Facts Upon Which the Method is Based. These metals are only slightly soluble in each other in the solid state, and do not form compounds with each other. The specific gravity of the ordinary tetragonal modification of tin, which is stable between 18° and 161°, is 7.29, and the specific volume is therefore 0.1371. The specific gravity of lead is 11.35 and its specific volume is therefore 0.08811. These values are affected but slightly by changes of several degrees in temperature.

If the specific volumes of these alloys are linear functions of their percentage composition it should be possible to analyze any such alloy whose specific volume V is known by use of the formula

$$x = \frac{100\,(V - 0.08811)}{0.1371 - 0.08811},$$

where x is the percentage of tin present by volume.

Experimental work has shown that this relation is only approximately correct; the departures found, which are sometimes positive and sometimes negative, do not exceed nine-tenths of 1 per cent, and the method is used where speed is more important than accuracy.

Outline of the Method of Procedure. Select a lump of the alloy which weighs from 10 to 15 gm. and weigh accurately. Wrap one end of a piece of aluminum wire around the lump so that it can be suspended by it. Place the specimen in a small beaker con-

taining distilled water, heat the latter to the boiling point and boil for about 3 minutes. Allow to cool to a temperature of 20° without removing the sample, then support the beaker on the wooden bridge with which the balance is supplied and suspend the specimen from the hook attached to the balance beam as shown in Fig. 67. Determine the weight necessary to counterbalance the specimen. Remove the specimen from the supporting wire and determine the weight necessary to counterbalance the latter when immersed to the point previously reached and subtract the result from the weight previously found.

Calculate the specific gravity from the formula given on page 358, assuming $G = 1$, the volume percentage of tin from the formula given in the preceding paragraph, and finally the weight percentage of tin.

III. Determination of Sulfuric Acid in a Commercial Sample

Facts Upon Which the Method is Based. The relation between the percentage composition and the specific gravity of aqueous solutions of sulfuric acid is represented by a curve, which differs but slightly from a straight line over the interval between zero and 80 per cent. For much of this interval the percentage can be calculated from the specific gravity by simple formulæ; between 66 and 81 per cent it can be calculated with great accuracy by multiplying by 86 and subtracting 68.82. Beyond 80 per cent the specific gravity increases at a rate which decreases continuously and beyond 97 per cent the specific gravity begins to decrease. The amounts of impurities present in commercial samples are usually too small to affect its specific gravity greatly.

Outline of Method of Procedure. Procure a set of hydrometers calibrated to determine specific gravities at $\left(\frac{15°}{4°}\right)$C. Fill a clean, dry, glass cylinder, whose inner diameter is at least twice

that of the hydrometers, about two-thirds full of the sample and bring to a temperature of 15° by immersing in warm or cold water and stirring with a thermometer. Choose the proper hydrometer of the set, which may necessitate several preliminary experiments, and allow it to sink gradually in the acid but avoid allowing any of the acid to touch the hydrometer above the point to which it finally sinks, and keep it in the center of the cylinder. Place the eye slightly below the level of the acid and read the point at which the plane representing the surface of the liquid intersects the scale of the hydrometer.

Remove the hydrometer from the cylinder, rinse it off under the tap and wipe dry. Return the acid to the sample bottle, rinse out the cylinder and wipe it dry. Calculate the percentage of sulfuric acid present by use of the table on pages 391–392.

IV. Determination of the Specific Gravity of Crude Petroleum

Facts Upon Which the Determination is Based. In the commercial evaluation of crude petroleum much importance is attached to its specific gravity. This is a consequence of the fact that the more valuable saturated hydrocarbons of low atomic weight are much lighter than the less valuable olefines, napthenes, and asphalt, and hence the specific gravity of the sample indicates roughly the value of the products which can be obtained from it when refined.

Thru long-established custom the Baumé hydrometer, for liquids lighter than water, is generally used in America in the petroleum industry in expressing the gravity of both the crude oil and the various products, gasolenes, kerosenes, lubricating oils, which are prepared from it. The high viscosity of many samples of crude oil, and its opacity, often make an accurate determination of the specific gravity difficult. The effect of temperature on the specific gravity is very large, and all determinations should be made at 60° F. (15.56° C.) for which the hydrometer is calibrated.

Outline of Method of Procedure. Test the temperature of the sample and if necessary place the bottle containing it in a vessel of warm or cold water, and stir the petroleum with a thermometer until the latter registers 15.56° C. Pour a sufficient amount of the sample into a clean, dry, glass cylinder, whose diameter is at least twice that of the hydrometer to be used, and fill it about two-thirds full. Allow the hydrometer, which should be clean and dry, to sink slowly in the petroleum until it comes to rest. Place the eye on a level with the liquid and sight across this level to the stem of the hydrometer, that is, endeavor to read the point corresponding to the level of the liquid, not the point to which some of the liquid is drawn on the stem by surface tension. Report the result in Baumé degrees and absolute specific gravity.

V. Questions and Problems. Series 26

1. Calculate the modulus of a hydrometer which sank to a point marked zero in water and to a point marked 50 in a solution containing seventy per cent of sulfuric acid. *Ans.* 131.1.

2. Specify dimensions for a hydrometer which could be used to determine specific gravities ranging from 1.4000 to 1.4200, and for which each unit in the fourth decimal place corresponds to 1 mm. on the scale.

Ans. Stem 4 mm. in diameter and 220 in length, bulb 4 cm. in diameter and 14 in length, weight 249.82 gm.

3. A sample of hydrochloric acid gave a reading of 16 on an American Baumé hydrometer. What would be the reading if a Brix hydrometer was placed in it? *Ans.* 44.12.

4. What volume of sulfuric acid of specific gravity 1.8 must be added to 100 cc. of 65 per cent acid to make it 75 per cent? *Ans.* 72.72 cc.

5. If a Twaddle hydrometer is placed in 80 per cent sulfuric acid, what would it read?

6. Plot a curve showing the relation of specific gravity to percentage composition for the lead-tin alloys.

7. Indicate the probable form of the curve representing the relation of specific gravity to percentage composition of lead-tin alloys if it is assumed that a compound of the formula $PbSn_2$ is formed.

8. A piece of metallic silver weighed 20 gm. in air, 18.1007 in water and 18.3818 in a sample of gasolene, what is the specific gravity of the gasolene?

CHAPTER L

COLORIMETRIC PROCESSES

I. General Features of Colorimetric Processes

Principle Involved. Certain substances, when dissolved in an appropriate solvent, yield solutions which show a characteristic color absorption when viewed by transmitted light, and it becomes possible to determine the concentration of such solutions by comparing the intensity of this absorption with that of a solution containing a known concentration of the substance concerned. A large number of quantitative processes are based upon this principle and are designated as "colorimetric" processes. They depend upon the measurement of a physical property, but the property here concerned is a complex one, and cannot be determined and expressed numerically except by reference to a purely empirical standard, that is, a second solution of known concentration. As a consequence the methods used in carrying out such determinations closely resemble those used in volumetric processes; hence they are frequently classed as a separate group, rather than with the other physico-chemical processes.

The intensity of the shade of color transmitted by two solutions of the same solute in the same solvent depends upon the concentrations of the two solutions and the thickness of the two layers compared. Since the absorption may be due to the presence of either the undissociated molecule, or of one or more of the ions into which it dissociates, it is affected by all of the conditions which affect the dissociation of electrolytes. If the concentrations are such that the dissociation is complete, and if other changes, such as hydration, do not take place the intensity of absorption will be directly proportional to the concentration, but this is rarely true.

Methods of Making Colorimetric Determinations. All colorimetric processes involve varying the thickness, the volume, or the concentration of either the standard or the unknown solution until the two show an absorption of equal intensity; hence three types of method are possible.

In the first the volumes and concentrations remain constant, and the ratio between the thickness of the layers of the two solutions at which the absorption is equally intense, is measured. This type of method assumes that the intensity of absorption is directly proportional to the concentration, which, as shown in the preceding paragraph, is not necessarily correct. This type of method is but rarely used in actual practice, except for the purpose of making the final comparison between two solutions which possess approximately the same concentration, that is, it is frequently necessary to combine it with methods of the second or third type.

In the second type of method the thicknesses observed remain constant, and the ratio of the volumes of the two solutions at which the absorption is equally intense is measured.

In the third type the thicknesses observed and the volumes are kept constant, and the concentration of the standard solution is increased until it shows an absorption equal in intensity to that of the unknown solution.

Colorimeters. The relation between the colorific intensities of two solutions is determined by means of a "colorimeter." An inexpensive and for most purposes sufficiently accurate form of this instrument is that of Wolff, a diagram of which is represented in Fig. 69. It consists of two glass cylinders A and B, which are accurately calibrated, and provided with glass stopcocks by means of which the solutions contained by them can be drawn off; they are supported in a frame which holds them in the same position with respect to the mirror M. The light reflected from the mirror passes thru the solutions in the two cylinders and is combined by an optical device in such a manner that the two halves of the eyepiece are illuminated by light which has passed thru the two

cylinders. The cylinders are enclosed in a case which eliminates the disturbing action of light from other sources. In using this instrument the more concentrated solution is diluted until the colorific absorptions are nearly equal, and the exact relation of

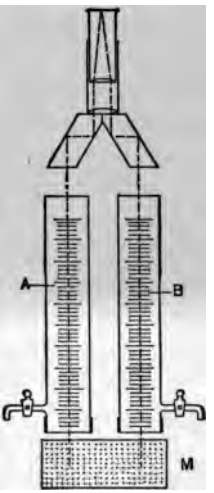

Fig. 69. — Wolff's Colorimeter

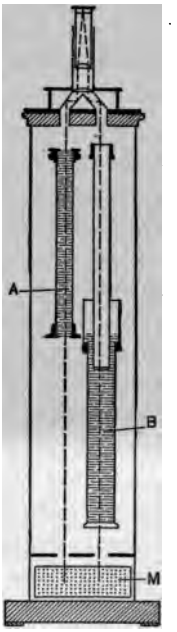

Fig. 70. — Stammar's Colorimeter

the two absorptions determined by reducing the thickness of the layer of the more concentrated solution until the two halves of the field of view show equal illumination.

A more expensive instrument is that of Stammar, a diagram of which is represented in Fig. 70. In this apparatus one of the two solutions is retained in a tube, which can be closed at both ends by plates of glass, held in position by means of rings which can be screwed onto the end of the tube; the other solution is retained

in a jar, which can be raised or lowered with respect to the base of the instrument by changing the position of the clamp which supports it. A glass piston, the end of which is flat and polished, projects into this jar, and by varying the position of the jar the thickness of the layer of liquid between the bottom of the piston and the bottom of the jar can be varied. The ratio of the thicknesses of the two solutions under observation can then be read off directly from the index fastened to the frame bearing the jar, with respect to the frame of the apparatus; its other features are essentially the same as those of the Wolff colorimeter.

Color Comparison Tubes. The second method of making a colorimetric determination is usually carried out in long narrow tubes, in one of which the more concentrated solution is diluted and mixed, until the colorific intensities are equal. The actual comparison is made in a box with darkened sides open at both ends; when in use one end is directed against the source of light employed, the other being the point of observation.

Nessler Cylinders. The third method is usually carried out in "Nessler tubes." They are made of clear, colorless glass, of an equal and uniform diameter with flat smooth bottoms. They are provided with marks corresponding to volumes of 50, 100, 150 or 200 cc. In using them the solution whose concentration is to be estimated is diluted to one of the four standard volumes, and a standard prepared in a companion cylinder, by adding to it a sufficient amount of an accurately standardized solution of the substance which is being estimated, to give at the same volume an equal color absorption. The amount of substance present is then calculated from the volume of the standard solution used and its concentration.

Where a large number of such determinations are being made, or where they are part of a daily routine, it is desirable to prepare a permanent series of color standards of a sufficiently wide range of concentrations. Where these are prepared it is preferable to substitute a bottle of uniform diameter for the cylindrical tubes.

Limitations of Colorimetric Methods. The actual percentage error involved in making a colorimetric comparison is rather large, unless an elaborate colorimeter is used and especially favorable conditions can be maintained. Very slight differences in the character of the light absorbed by the two solutions, which may result from the presence of small amounts of other substances in the sample being analyzed, increase the percentage error materially, altho in such instances the effort is usually made to avoid the difficulty by introducing approximately equal amounts of these substances in the prepared standards. Slight differences in the thickness or absorption capacity of the glass vessels used to retain the solutions exercise a disturbing influence; also, the personal qualifications of the analyst, that is, his ability to distinguish color shades, has an unusually large effect upon the results obtained.

Experience proves that with most colorific substances there is a certain range of concentrations at which the color shades change most decidedly with the concentration, and the percentage error of the comparison may be large unless made within this range. The kind of light used in making the comparison is also a factor; usually pure white light, such as is reflected from a white opaque, or translucent mirror, gives the best results.

With most of the colorimetric processes in common use the final comparison must be made with solutions containing a very small concentration of the colored compound, and the percentage error of the process is sufficiently small only when the total amount of the substance which is being estimated is small. Hence colorimetric processes are in general poorly adapted to the analysis of substances containing large percentages of the element or compound concerned, for altho the amount of substances actually determined may be made small by using a very small weight of the sample, or by taking a small fraction of the solution first prepared, the error concerned in the final comparison is then multiplied sufficiently to give a large departure in the final result.

On the other hand, colorimetric processes are peculiarly adapted

to the determination of small percentages of many elements and compounds. Usually previous separation of the constituent which is being determined is unnecessary, and in many cases amounts which are entirely too small to be estimated by any other class of methods can be determined colorimetrically with a satisfactory percentage accuracy. A very large number of such processes have been elaborated and are in general use.*

II. Determination of Manganese in Cast Iron and Steel

Colorific Power of Permanganates. Solutions which contain the permanganic ion $\overline{Mn}O_4$ possess a deep red or pink color, the intensity of which is approximately proportional to the concentration; hence the amount of manganese present in this form can be accurately determined by comparing the color of the unknown with that of a standard permanganate solution. If the comparison is made in tubes containing a layer of solution 100 mm. in thickness the best results are obtained when the concentration is in the neighborhood of 10 mg. of manganese per liter. As the permanganic ion is readily reduced by organic matter or even by light the solutions compared fade appreciably on long standing, unless oxidizing agents of sufficient strength are also present.

The Formation of Permanganates. The complete conversion of the manganous ion into the permanganic ion can be effected by certain oxidizing agents, but only in the absence of hydrochloric acid, and in the presence of a large concentration of nitric acid. Lead peroxide and sodium bismuthate are often employed for this purpose, but a more convenient reagent to use is ammonium or potassium persulfate, the action of which can be represented by the expression:

$$5\,(NH_4)_2S_2O_8 + 2\,Mn(NO_3)_2 + 8\,H_2O \rightarrow 5\,(NH_4)_2SO_4 + 2\,HMnO_4 + 5\,H_2SO_4 + 4\,NHO_3.$$

The speed of this reaction under ordinary conditions is not great

* See Schreiner, Jour. of the Am. Chem. Soc., **27**, 1192 (1903).

but in the presence of a silver salt and at a temperature above 70° it progresses rapidly. The function of the silver salt seems to be that of a catalyzer; in its absence some of the manganese may separate as the dioxide.

Application of the Method. This method is especially useful in the estimation of the small amounts of manganese found in the commercial alloys of iron and in iron ores. In applying the method to such determinations the error resulting from the color imparted to the solution by the ferric ions present and that due to the color which results from the partial oxidation of the carbon of iron carbide by the nitric acid usually employed to dissolve such alloys must be considered. The colorific power of the ferric ion, especially in a nitric acid solution, and at ordinary temperatures, is extremely small as compared with that of the permanganic ion, and even though the percentage of iron is one hundred times as great as that of manganese, it modifies to a slight degree only the color resulting from the permanganate ion. The color due to carbon, especially in the analysis of steels containing a large percentage of carbon, is a more important item, but the difficulty is eliminated if the precaution is taken to treat the solution with an excess of some oxidizing agent, such as ammonium persulfate, which slowly oxidizes the carbon to carbon dioxide. Actual experience with the process shows that it is scarcely possible to prepare a solution of the sample containing all of the manganese as permanganate, which possesses exactly the same color shade as a pure solution of a soluble permanganate. It is preferable, therefore, to prepare the color standard used from an alloy or ore, whose manganese content has been previously determined with great accuracy, preferably from a sample in which the ratio of iron to manganese is approximately the same as that in the sample under consideration.

In the analysis of samples of gray cast iron, a fine black residue representing carbon and silicon, which remains insoluble, also interferes with the color comparison and makes filtration neces-

sary. The entire process is a simple one and under favorable conditions a determination can be made within one half hour.

Outline of Method of Procedure. Weigh out 0.2 gm. of the standard, the manganese content of which is accurately known, and an equal amount of the unknown sample and place in test tubes, which have a capacity of 70 cc. Add to both tubes 10 cc. of dilute nitric acid, and warm both in a water bath until complete decomposition has been effected and oxides of nitrogen are no longer evolved, then add about one half gram of ammonium persulfate and continue heating with occasional shaking until oxygen is no longer given off. If a large amount of carbon remains in either tube, that is, if either sample contains much graphitic carbon, filter through a small 7 cm. filter into a second test tube and wash the filter with about 10 cc. of water. Next dilute both solutions to a volume of 20 cc., add 10 cc. of reagent silver nitrate solution and then 1 gm. of ammonium persulfate. Place both tubes in the water bath and allow to remain with occasional shaking until the maximum amount of red color is developed, which should not require more than five minutes.

Cool both tubes by means of a stream from the water tap, transfer to 200 cc. graduated flasks and dilute both to exactly that volume. If one of the two solutions shows a much greater color absorption than the other dilute the former to exactly 300, 400 or 500 cc., that is, until the color absorption of the two solutions does not differ greatly.

Transfer a portion of the solution which has the less intense color to a color comparison cylinder, preferably of the Stammer or Wolff type, using sufficient to give a layer which is from 100 to 150 mm. in thickness; transfer a somewhat smaller amount of the second solution to the other cylinder of the apparatus. Adjust the arm which sustains the second cylinder, if a Stammar colorimeter is used, or the thickness of the solution in the second cylinder, if a Wolff apparatus is used, until no difference can be detected in the amount of absorption in the two cylinders and ascertain the com-

parative depths of solution observed. Repeat the adjustment and observation at least twice more and take the mean of the three as the final correct result.

Calculate the percentage of manganese present from the per cent of Mn in the standard sample, the volumes to which the two solutions were diluted and depths of the layers which gave equal color absorptions.

III. Determination of Copper in a Copper Slag

Properties of the Cupric-Ammonium Ion. Whenever an excess of ammonium hydroxide is added to a solution containing cupric salt an intense blue color is produced, owing to the formation of the cupric ammonium ion. This ion is usually represented by the formula $\overset{+}{Cu}(\overset{+}{NH_3})_4$, but ions having the formulas $\overset{+}{Cu}(\overset{+}{NH_3})_5$ and $\overset{+}{Cu}(\overset{+}{NH_3})_6$ are believed to be present in small amounts in such solutions. Its colorific power can be inferred from the fact that 1 mg. of copper in this form imparts a color to 100 cc. of water, which can be recognized in layers of solution 8 cm. in thickness. The intensity of the color increases with increasing concentration at a fairly uniform rate up to values some twenty times as great as the minimum given.

Apparently the intensity of the color of such solutions is affected to some extent by the nature of the anions, and the concentration of the ammonium salts and ammonium hydroxide present in the solution; hence all comparisons should be made with solutions of approximately the same composition. It has also been found that the colorific intensity of such solutions remains unchanged, even after long standing, if it contains SO_4 rather than NO_3 ions. In using the method it is customary to prepare a series of color standards with which the solution to be tested is compared.

Decomposition of Copper Slags. Copper slags which have been "chilled," that is, suddenly cooled by dropping the molten

slag from the furnace into cold water, and which have been finely ground, can be readily and completely decomposed by strong hydrochloric acid. If the sample is stirred constantly during the decomposition, and diluted as soon as this has been completed, it is possible to avoid the separation of gelatinous silica; further, all the copper can be precipitated from this diluted solution by means of hydrogen sulfide, and all of it separated from the iron, and other elements normally present. If the proper conditions are not complied with in making the decomposition some of the silica will separate in gelatinous form, and it then becomes necessary to dehydrate and separate all of the silica before the copper can be separated, which greatly increases the time required.

The percentage of copper normally present in blast furnace slags should not exceed 0.3 per cent; "converter" slags may contain as much as 2.5 per cent. The colorimetric method is especially adapted to the analysis of such products, owing to its simplicity and speed; its accuracy is not sufficient to make it a satisfactory method for the evaluation of copper ores.

Preparation of a Series of Color Standards. Weigh out exactly 0.2 gm. of pure copper foil, place in a 200 cc. flask, add 20 cc. of dilute nitric acid, warm gently until the copper is dissolved, then evaporate to about 10 cc. Dilute the solution to 50 cc., transfer to a graduated liter flask, add 200 cc. of reagent ammonium hydroxide, allow to cool and dilute to the mark in the flask. Procure and carefully clean six 150 cc. bottles made from clear, colorless glass, whose cross section is represented by a square. To the first of these add exactly 50 cc. of the copper solution and dilute to exactly 100 cc. with a mixture of one volume of ammonium hydroxide and three of water. To the second add 40 cc. of copper solution and sufficient diluted ammonium hydroxide to make a volume of 100 cc. and in the preparation of each succeeding standard reduce the volume of the copper solution by 10 cc. and increase the volume of diluted ammonium hydroxide by the same amount.

Outline of Method of Procedure. Crush the sample until fine enough to pass thru a 100-mesh sieve. Weigh out 2 gm. into a 200 cc. beaker, add 10 cc. of water and stir until all of the particles are moistened, then add 8 cc. of concentrated hydrochloric acid and stir continuously for 5 minutes, or until the undissolved residue is black and flocculent, and remains for the most part suspended in the liquid.

Add to the mixture, without further delay, 70 cc. of hydrogen sulfide water, or add that amount of water and saturate with the gas. Warm for a few minutes or until the precipitated copper sulfide coagulates, then filter thru a Witt filter and wash twice with 10 cc. of water.

Transfer the asbestos filter and adhering precipitate to the beaker used for the decomposition, rinse out the filter tube with 5 cc. of concentrated nitric acid, receiving the rinsings in the beaker, and warm the mixture until all of the copper sulfide present has been brought into solution. Add to the mixture 30 cc. of reagent ammonium hydroxide, heat to about 60° and filter thru a Witt filter, which has been well washed from adhering fibers, and wash twice with 10 cc. portions of dilute ammonium hydroxide.

Transfer the filtrate to a bottle similar to those used for the preparation of the color standards. Compare the color of this bottle with that of the standards and ascertain to which one it is equivalent. Calculate the percentage of copper present from the weight of copper in the standard bottle finally chosen and the weight of sample used.

	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4 8 13	17 21 25	29 33 38
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4 8 11	15 19 23	26 30 34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3 7 10	14 17 21	24 28 31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3 6 10	13 16 19	23 26 29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3 6 9	12 15 18	21 24 27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3 6 8	11 14 17	20 22 25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3 5 8	11 13 16	18 21 24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2 5 7	10 12 15	17 20 22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2 5 7	9 12 14	16 19 21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2 4 7	9 11 13	16 18 20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2 4 6	8 11 13	15 17 19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2 4 6	8 10 12	14 16 18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2 4 6	8 10 12	14 15 17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2 4 6	7 9 11	13 15 17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2 4 5	7 9 11	12 14 16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2 3 5	7 9 10	12 14 15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2 3 5	7 8 10	11 13 15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2 3 5	6 8 9	11 13 14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2 3 5	6 8 9	11 12 14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1 3 4	6 7 9	10 12 13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1 3 4	6 7 9	10 11 13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1 3 4	6 7 8	10 11 12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1 3 4	5 7 8	9 11 12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1 3 4	5 6 8	9 10 12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1 3 4	5 6 8	9 10 11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1 2 4	5 6 7	9 10 11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1 2 4	5 6 7	8 10 11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1 2 3	5 6 7	8 9 10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1 2 3	5 6 7	8 9 10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1 2 3	4 5 7	8 9 10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1 2 3	4 5 6	8 9 10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1 2 3	4 5 6	7 8 9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1 2 3	4 5 6	7 8 9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1 2 3	4 5 6	7 8 9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1 2 3	4 5 6	7 8 9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1 2 3	4 5 6	7 8 9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1 2 3	4 5 6	7 7 8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1 2 3	4 5 5	6 7 8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1 2 3	4 4 5	6 7 8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1 2 3	4 4 5	6 7 8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1 2 3	3 4 5	6 7 8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1 2 3	3 4 5	6 7 8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1 2 2	3 4 5	6 7 7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1 2 2	3 4 5	6 6 7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1 2 2	3 4 5	6 6 7

	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1 2 2	3 4 5	5 6 7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1 2 2	3 4 5	5 6 7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1 2 2	3 4 5	5 6 7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1 1 2	3 4 4	5 6 7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1 1 2	3 4 4	5 6 7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1 1 2	3 4 4	5 6 6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1 1 2	3 4 4	5 6 6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1 1 2	3 3 4	5 6 6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1 1 2	3 3 4	5 5 6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1 1 2	3 3 4	5 5 6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1 1 2	3 3 4	5 5 6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1 1 2	3 3 4	5 5 6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1 1 2	3 3 4	5 5 6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1 1 2	3 3 4	4 5 6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1 1 2	2 3 4	4 5 6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1 1 2	2 3 4	4 5 6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1 1 2	2 3 4	4 5 5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1 1 2	2 3 4	4 5 5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1 1 2	2 3 4	4 5 5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1 1 2	2 3 4	4 5 5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1 1 2	2 3 3	4 5 5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1 1 2	2 3 3	4 5 5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1 1 2	2 3 3	4 4 5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1 1 2	2 3 3	4 4 5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1 1 2	2 3 3	4 4 5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1 1 2	2 3 3	4 4 5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1 1 2	2 3 3	4 4 5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1 1 2	2 3 3	4 4 5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1 1 2	2 3 3	4 4 5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1 1 2	2 3 3	4 4 5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1 1 2	2 3 3	4 4 5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1 1 2	2 3 3	4 4 5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0 1 1	2 2 3	3 4 4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0 1 1	2 2 3	3 4 4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0 1 1	2 2 3	3 4 4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0 1 1	2 2 3	3 4 4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0 1 1	2 2 3	3 4 4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0 1 1	2 2 3	3 4 4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0 1 1	2 2 3	3 4 4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0 1 1	2 2 3	3 4 4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0 1 1	2 2 3	3 4 4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0 1 1	2 2 3	3 4 4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0 1 1	2 2 3	3 4 4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0 1 1	2 2 3	3 4 4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0 1 1	2 2 3	3 3 4

SPECIFIC GRAVITIES OF SULFURIC ACID

Lunge and Isler

Specific gravity $\frac{15°}{4°}$ in vacuo	100 parts by weight correspond to % H_2SO_4	Specific gravity $\frac{15°}{4°}$ in vacuo	100 parts by weight correspond to % H_2SO_4	Specific gravity $\frac{15°}{4°}$ in vacuo	100 parts by weight correspond to % H_2SO_4
1.000	0.09	1.205	27.95	1.410	51.15
1.005	0.83	1.210	28.58	1.415	51.66
1.010	1.57	1.215	29.21	1.420	52.15
1.015	2.30	1.220	29.84	1.425	52.63
1.020	3.03	1.225	30.48	1.430	53.11
1.025	3.76	1.230	31.11	1.435	53.59
1.030	4.49	1.235	31.70	1.440	54.07
1.035	5.23	1.240	32.28	1.445	54.55
1.040	5.96	1.245	32.86	1.450	55.03
1.045	6.67	1.250	33.43	1.455	55.50
1.050	7.37	1.255	34.00	1.460	55.97
1.055	8.07	1.260	34.57	1.465	56.43
1.060	8.77	1.265	35.14	1.470	56.90
1.065	9.47	1.270	35.71	1.475	57.37
1.070	10.19	1.275	36.29	1.480	57.83
1.075	10.90	1.280	36.87	1.485	58.28
1.080	11.60	1.285	37.45	1.490	58.74
1.085	12.30	1.290	38.03	1.495	59.22
1.090	12.99	1.295	38.61	1.500	59.70
1.095	13.67	1.300	39.19	1.505	60.18
1.100	14.35	1.305	39.77	1.510	60.65
1.105	15.03	1.310	40.35	1.515	61.12
1.110	15.71	1.315	40.93	1.520	61.59
1.115	16.36	1.320	41.50	1.525	62.06
1.120	17.01	1.325	42.08	1.530	62.53
1.125	17.66	1.330	42.66	1.535	63.00
1.130	18.31	1.335	43.20	1.540	63.43
1.135	18.96	1.340	43.74	1.545	63.85
1.140	19.61	1.345	44.28	1.550	64.26
1.145	20.26	1.350	44.82	1.555	64.67
1.150	20.91	1.355	45.35	1.560	65.08
1.155	21.55	1.360	45.88	1.565	65.49
1.160	22.19	1.365	46.41	1.570	65.90
1.165	22.83	1.370	46.94	1.575	66.30
1.170	23.47	1.375	47.47	1.580	66.71
1.175	24.12	1.380	48.00	1.585	67.13
1.180	24.76	1.385	48.53	1.590	67.59
1.185	25.40	1.390	49.06	1.595	68.05
1.190	26.04	1.395	49.59	1.600	68.51
1.195	26.68	1.400	50.11	1.605	68.97
1.200	27.32	1.405	50.63	1.610	69.43

SPECIFIC GRAVITIES OF SULFURIC ACID (*Continued*)

Specific gravity $\frac{15°}{4°}$ in vacuo	100 parts by weight correspond to % H_2SO_4	Specific gravity $\frac{15°}{4°}$ in vacuo	100 parts by weight correspond to % H_2SO_4	Specific gravity $\frac{15°}{4°}$ in vacuo	100 parts by weight correspond to % H_2SO_4
1.615	69.89	1.735	80.24	1.827	91.50
1.620	70.32	1.740	80.68	1.828	91.70
1.625	70.74	1.745	81.12	1.829	91.90
1.630	71.16	1.750	81.56	1.830	92.10
1.635	71.57	1.755	82.00	1.831	92.30
1.640	71.99	1.760	82.44	1.832	92.52
1.645	72.40	1.765	82.88	1.833	92.75
1.650	72.82	1.770	83.32	1.834	93.05
1.655	73.23	1.775	83.90	1.835	93.43
1.660	73.64	1.780	84.50	1.836	93.80
1.665	74.07	1.785	85.10	1.837	94.20
1.670	74.51	1.790	85.70	1.838	94.60
1.675	74.97	1.795	86.30	1.839	95.00
1.680	75.42	1.800	86.90	1.840	95.60
1.685	75.86	1.805	87.60	1.8405	95.95
1.690	76.30	1.810	88.30	1.8410	97.00
1.695	76.73	1.815	89.05	1.8415	97.70
1.700	77.17	1.820	90.05	1.8410	98.20
1.705	77.60	1.821	90.20	1.8405	98.70
1.710	78.04	1.822	90.40	1.8400	99.20
1.715	78.48	1.823	90.60	1.8395	99.45
1.720	78.92	1.824	90.80	1.8390	99.70
1.725	79.36	1.825	91.00	1.8385	99.95
1.730	79.80	1.826	91.25		

List of Apparatus Needed

The articles which are named in the following list represent the apparatus with which it is desirable that each student should be provided; it can be modified in many particulars without jeopardizing the success of his work. For many of the determinations which are described, especially those outlined in Chapters XII, XIII, XIV, XV, XXII, XXVII, XXX, XXXI, XXXIII, XXXIV, XLIX and L, additional apparatus is necessary. It will be found desirable to prepare a series of boxes containing all of the special articles needed for each of these determinations and give them out to the different students as called for.

6 Beakers of Jena glass with lips, 2–100 cc., 2–250 cc., 2–400 cc., 1–600 cc., 1–800 cc.
2 Bottles with glass stoppers, 2000 cc.
2 Burets, 50 cc. (1 Mohr form and 1 Geissler form.)
1 Bunsen burner with rubber tubing.
1 Camel's hair brush.
2 Clamps to hold burets.
1 Desiccator with support for crucibles.
4 Erlenmeyer flasks, 2–100 cc., 2–250 cc.
1 Filter flask with rubber stopper, 500 cc.
2 Filter holders (to fit cleats on desk).
1 Package washed filters, 25–11 cm., 20–9 cm., 10–7 cm.
1 Flask of Jena glass, 750 cc., with 2-hole rubber stopper for wash bottle.
1 Flask of Jena glass, 250 cc., with 2-hole rubber stopper for wash bottle.
1 Pair forceps of nickel or brass.
4 Funnels, 2–5 cm., 2–8 cm.
1 Glass filter tube.
4 Feet glass tubing, 6 mm. in diameter.
3 Glass rods, 20 cm. long, 6 mm. in diameter.
1 Piece glazed paper, 30 cm. square.
1 Graduated cylinder, 50 cc.
1 Iron stand with two rings.
2 Keys, 1 for desk and 1 for drawer to balance.
3 Pipets, 1–5 cc., 1–10 cc., 1–25 cc.
1 Piece platinum wire, 20 cm. long and 0.2 mm. in diameter.
4 Porcelain crucibles, 2–No. 000 (8 cm.), 2–No. 00 (12 cc.).
1 Porcelain Gooch crucible, 25 cc.
1 Porcelain plate.
2 Porcelain casseroles or evaporating dishes, 250 cc.
1 Piece fine rubber tubing, 20 cm. long and 6 mm. in diameter.
4 Reagent bottles, for dilute acids and ammonium hydroxide.
4 Test tubes, 15 cm.
2 Triangles of nichrome wire.
2 Weighing bottles, 10 cm. and 30 cm.
2 Pieces of wire gauze.
1 Witt filter plate, 23 mm.

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